SYNTHETIC AND MECHANISTIC STUDIES IN POLYNITROAROMATIC CHEMISTRY

Roger Myrry King

Submitted to the Council for National Academic Awards for the degree of Doctor of Philosophy in partial fulfilment of the requirements for this degree.

The research was conducted at Sheffield City Polytechnic in collaboration with the Ministry of Defence, Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey.

January 1982

ACKNOWLEDGEMENTS

I am very grateful to Dr. George Corfield for his guidance throughout this work and to Dr. Gerard Hayes and Dr. Peter Golding of the Ministry of Defence who provided many of the materials I needed and a lot of useful advice. My thanks are also due to the staff of the Department of Chemistry, Sheffield City Polytechnic and Dr. Michael Crampton, Durham University for their assistance and helpful discussions. None of this work could have been done but for a grant from the Science Research Council Co-operative Awards in Science and Engineering scheme for which I am most grateful. Finally I would like to thank Mrs. Lorna Howarth for her painstaking work in converting my tangled manuscript into an orderly typescript.

ABBREVIATIONS

DMF	dimethylformamide
DMSO	dimethylsulphoxide
DNB	1,3-dinitrobenzene
DNBB	4,4'-dinitrobibenzyl
DNS	4,4'-dinitrostilbene
E	extinction coefficient
EDA	ethylenediamine
ESR	electron spin resonance
HMPA	hexamethylphosphoramide
HNBB	2,2',4,4',6,6'-hexanitrobibenzyl
^{1}HNMR	proton nuclear magnetic resonance
HNS	2,2',4,4',6,6'-hexanitrostilbene
HPLC	high performance liquid chromatography
PERME	Propellants, Explosives and Rocket Motor Establishment
TEAP	tetraethylammonium perchlorate
THF	tetrahydrofuran
TLC	thin layer chromatography
TNB	1,3,5-trinitrobenzene
TNBCl	2,4,6-trinitrobenzyl chloride
$TNBCl^-$	2,4,6-trinitrobenzyl chloride anion
TNT	2,4,6-trinitrotoluene
TNT^-	2,4,6-trinitrobenzyl anion
$TNT^{\cdot-}$	2,4,6-trinitrotoluene radical anion

IN POLYNITROAROMATIC CHEMISTRY

Roger Myrry KING

ABSTRACT

2,2',4,4',6,6' - Hexanitrostilbene (HNS) is a heat resistant explosive which is also important as a crystal growth modifier for melt-cast TNT. This work has studied a new method of preparation of HNS, by catalytic oxidation of TNT, to identify the parameters which are significant and to contribute to an understanding of the mechanism involved.

A typical reaction is marked by several colour changes, from brown to purple to red-brown then blue. Visible and ^{1}HNMR spectroscopy, hydrogen-deuterium exchange experiments and electrochemical methods have been used to identify intermediates involved in the reaction. The colours have been assigned to a 3- σ-complex of TNT, the trinitrobenzyl anion, 3- σ- and 1- σ-complexes of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) and the HNS radical anion respectively. ^{1}HNMR implied the presence of radicals in the system. It was also shown that HNS can form a σ-complex on reaction with base and that HNBB will ionise in basic solution with loss of an aromatic proton.

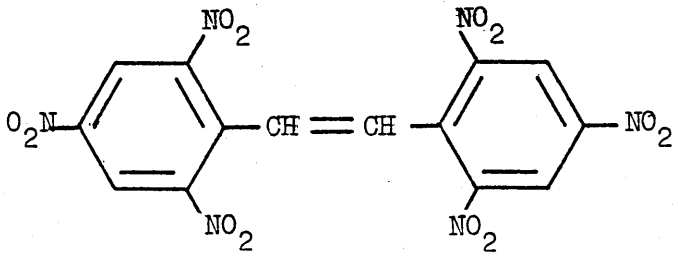
HNBB was the main product of the catalytic oxidation of TNT at room temperature, with HNS produced when the reaction mixture was warmed to 55°C. Without catalyst the yield of HNBB and HNS was poor and a more complex mixture of by-products resulted. Oxygen was vital for a good yield of HNBB, a polar, aprotic solvent was also important. The best yield of HNBB came from using sodium methoxide as base in an equimolar amount with TNT. Of the catalysts investigated, a copper sulphate-pyridine slurry was preferred. Dehydrogenation of HNBB to HNS required less base than the oxidation of TNT to HNBB and proceeded without oxygen. The catalytic oxidation of TNT to HNS showed no particular advantages over the established process of HNS production.

A probable pathway for the oxidation reaction was proposed which involved a radical mechanism with electron transfer from the trinitrobenzyl anion to an electron acceptor.

CONTENTS

1. INTRODUCTION

The work presented in this thesis developed from collaboration between the Department of Chemistry, Sheffield City Polytechnic and the Ministry of Defence, Propellants, Explosives and Rocket Motor Establishment (PERME), Waltham Abbey, where there is a general interest in the chemistry of polynitroaromatic compounds. Of particular interest is the chemistry of 2,2',4,4',6,6' - hexanitrostilbene (HNS, 1).



(1)

1.1 2,2',4,4',6,6' - Hexanitrostilbene

HNS is a heat-resistant explosive which has also found an important use as a crystal growth modifier in melt-cast trinitrotoluene charges.

1.1.1 Heat-Resistant Explosives

Conventional explosives cannot withstand the high temperatures and low pressures involved in operations such as stage separation in rockets and missiles and ejecting pilots from aircraft, unless special insulation and sealing are used. This puts weight and volume restrictions on the design of the equipment. It also raises questions of safety and reliability, because insulation may break or seals leak.

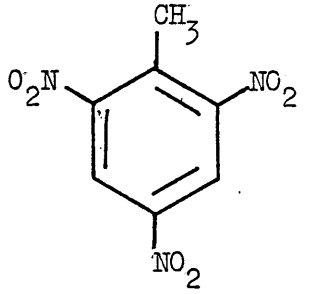
It is better to use an explosive that can withstand extremes of temperature and pressure without special precautions. HNS is such an explosive and has been used in the F-111 aircraft and in the Gemini and Apollo space rockets. A mixture of HNS and Teflon binder was used

in the preparation of large explosive charges for the Apollo Lunar Surface Experimental Package. [1,2]

There is also a great need in industry for explosives which are stable, safe and reliable at high temperatures. For example, explosives are sometimes used in oil wells where the temperature may be as high as 300°C. Explosive charges are used in the steel industry to tap furnaces in which the temperature of the tap hole may be over 500°C. Conventional explosive charges must have heavy insulation to perform such jobs and even then the charge must be initiated within 3 or 4 minutes or it may fail due to thermal instability. HNS is one of a range of nitro compounds which have been found to be useful as heat-resistant explosives. [3]

1.1.2 The Stability of 2,4,6 - Trinitrotoluene Charges

2,4,6 - Trinitrotoluene (TNT, 2) is still the major explosive used by the military, either on its own or in combination with other explosives.



(2)

Its importance lies in its relative insensitivity to shock and its convenient melting point, around 80°C, which means it can be melted by steam and cast into shells, or slurried with other explosives and then cast. The main short-comings of TNT as an explosive are that it is very insensitive in the cast form, it is difficult to cast without air holes and as molten TNT cools in a shell it undergoes orientated crystal growth which produces cracks in the charge. Cracks in the high

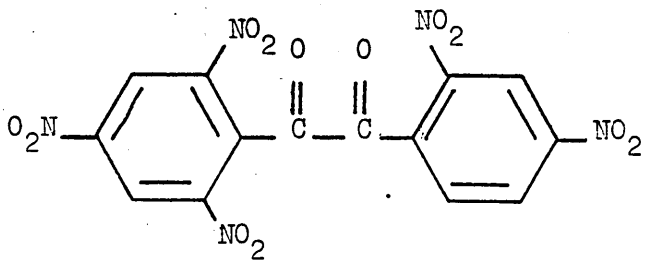
explosive filling of a shell increase the likelihood of initiation of a premature explosion under the extremely high forces encountered during gun firing.

A small amount of HNS, about 0.5% $^{w}/_{v}$, dissolved in molten TNT promotes unorientated crystal growth as the TNT solidifies to give a crack-free charge. [4] A cycle-cast method is used in which a small amount of HNS is heated in TNT to 100°C, the solution stirred and then solidified. This mixture is then remelted, taking care that the melt temperature does not exceed 85°C. Resolidification now produces a cast consisting of very fine, randomly orientated grains.

Crystallographic studies[5] have established strong similarities between the structures of HNS and TNT and this correspondence is believed to be important to the observed ability of HNS to induce crystallisation in molten TNT. There is evidence to suggest that HNS forms a complex with TNT of composition $(TNT)_2$ HNS and that this is the active nucleating agent. [6,7]

1.2 The Synthesis of Nitrostilbenes

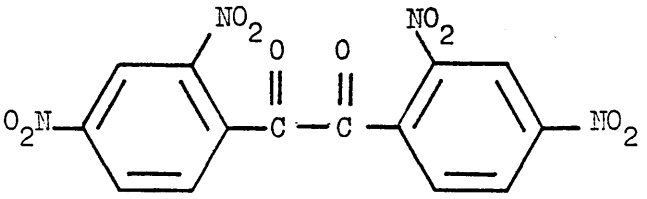
Direct nitration of stilbene does not give its nitro derivatives because the double bond is vulnerable to oxidation. Nitration of 2,4,6 - trinitrostilbene with a mixture of nitric and sulphuric acid at 100°C for 2 hours yielded 2,4,6,2',4' - pentanitrostilbene. [8] A stronger nitrating mixture of anhydrous nitric acid and sulphuric acid gave 2,4,6,2',4' - pentanitrobenzil (3).



(3)

Nitration of 2,2',4,4' - tetranitrostilbene with nitric acid, sulphuric acid and oleum on a steam bath for 7 hours gave 2,2',4,4' -

tetranitrobenzil[9] (4).



(4)

Nitrostilbenes have been prepared by the condensation of nitrotoluenes with benzaldehyde and its derivatives. Heating 2,4 - dinitrotoluene with 2-, 3- or 4-nitrobenzaldehyde yielded the corresponding isomer of trinitrostilbene[10] (eqn 1).

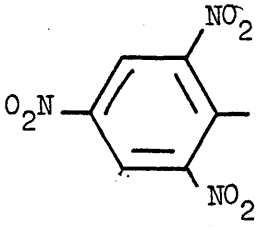
$$CH_3C_6H_3(NO_2)_2 + OHCC_6H_4NO_2 \xrightarrow[160^oC]{\text{piperidine}} (NO_2)_2C_6H_3CH = CHC_6H_4NO_2$$

(eqn 1)

A similar reaction between TNT and 4-nitrobenzaldehyde was used to prepare 2,4,6,4' - tetranitrostilbene[11] (eqn 2).

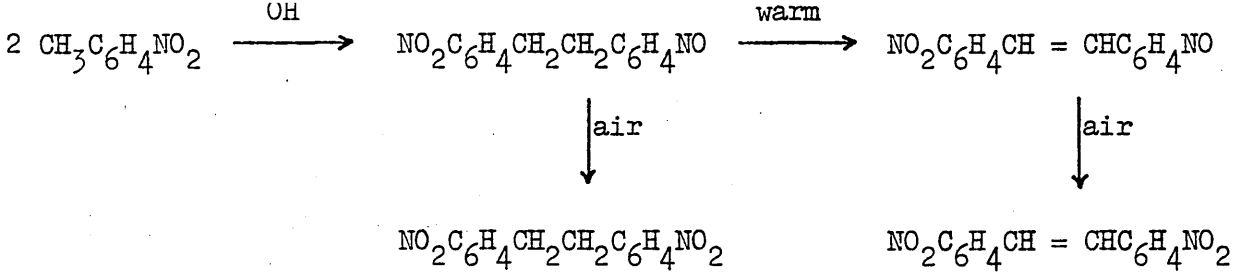
$$PiCH_3 + OHCC_6H_4NO_2 \xrightarrow{\text{piperidine}} PiCH = CHC_6H_4NO_2$$

(eqn 2)

Pi = 

Condensation of TNT with trinitrobenzaldehyde produced only a poor yield of HNS[12].

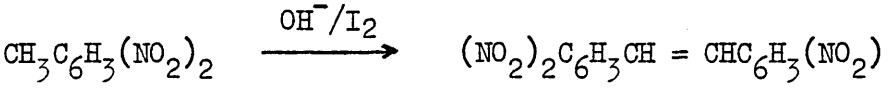
4,4' - Dinitrobibenzyl was prepared by oxidation of 4-nitrotoluene in methanolic potassium hydroxide[13]. Warming the reaction mixture produced 4,4' - dinitrostilbene. The reaction was thought to involve oxidation of a nitroso intermediate (eqn 3).



(eqn 3)

More recent work has established that the reaction involves ionisation of the nitrotoluene and formation of the nitrotoluene radical anion[14].

When the same reaction was tried with 2,4 - dinitrotoluene a complicated brown condensation product resulted[13]. The synthesis of 2,2',4,4' - tetranitrostilbene was achieved by using an alkaline solution of iodine at low temperature (eqn 4).



(eqn 4)

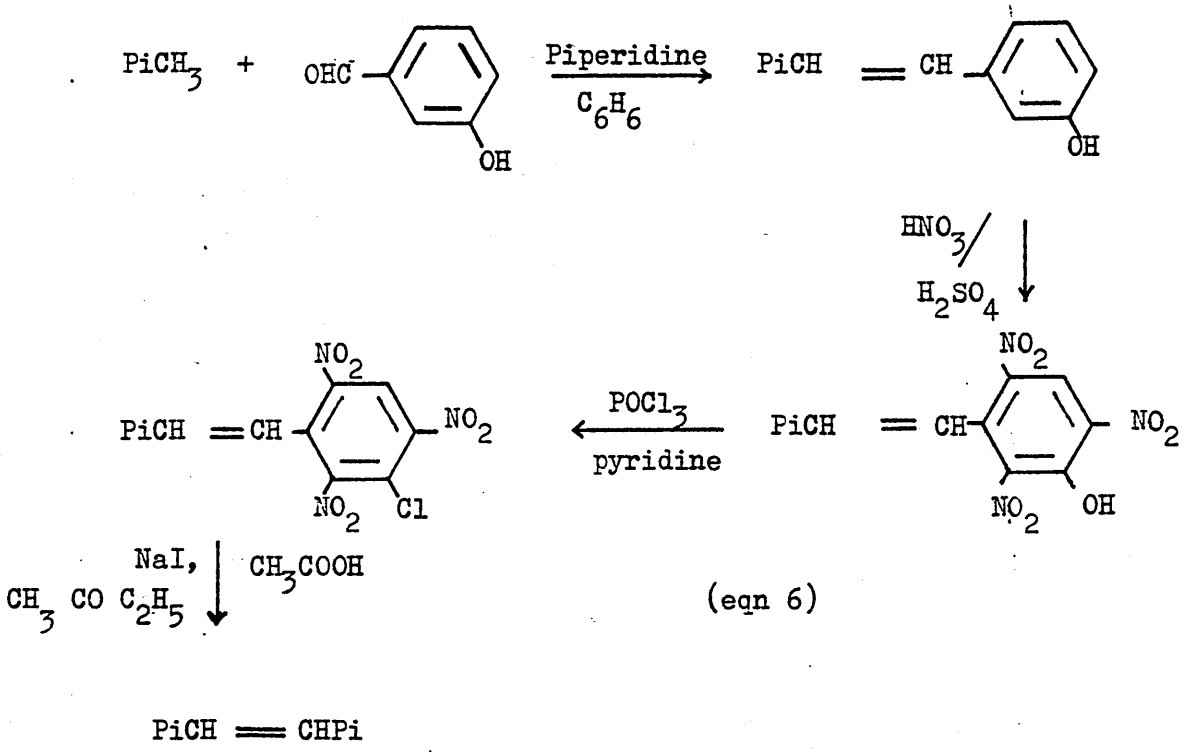
A similar reaction with TNT yielded less than 5% HNS[12].

A crystalline product, melting point 211°C, from the reaction of 2,4,6 - trinitrobenzyl bromide with alcoholic potassium hydroxide was assumed to be HNS[15]. When this procedure was later repeated by Shipp[12] the results were different. Shipp obtained no product similar to that originally reported. However, she did obtain a product, melting point 316°C, from the reaction of 2,4,6 - trinitrobenzyl chloride with alcoholic potassium hydroxide (eqn 5).

$$2\ PiCH_2Cl \xrightarrow[CH_3OH]{KOH} PiCH = CH\ Pi$$

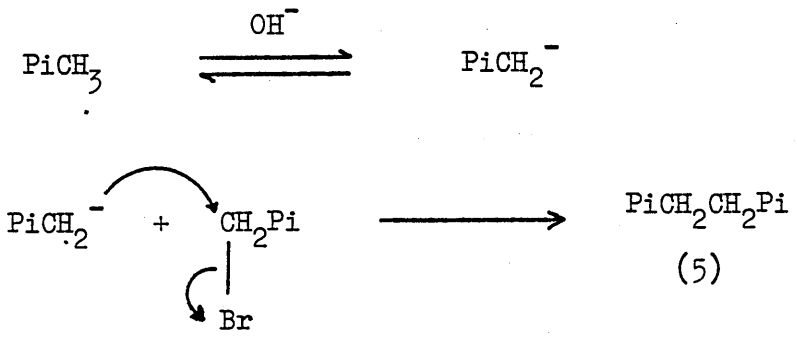
(eqn 5)

That this product was HNS was confirmed by molecular weight determination, elemental analyses and by an unambiguous independent synthesis (eqn 6).



(eqn 6)

The product, melting point 211°C, from the original reaction of 2,4,6-trinitrobenzyl bromide with base, was assumed by Shipp to be 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB, 5). It was thought to be produced by a nucleophilic displacement reaction by the 2,4,6-trinitrobenzyl anion on the bromide[16] (eqn 7).



(eqn 7)

The source of the anion was residual TNT in the bromide.

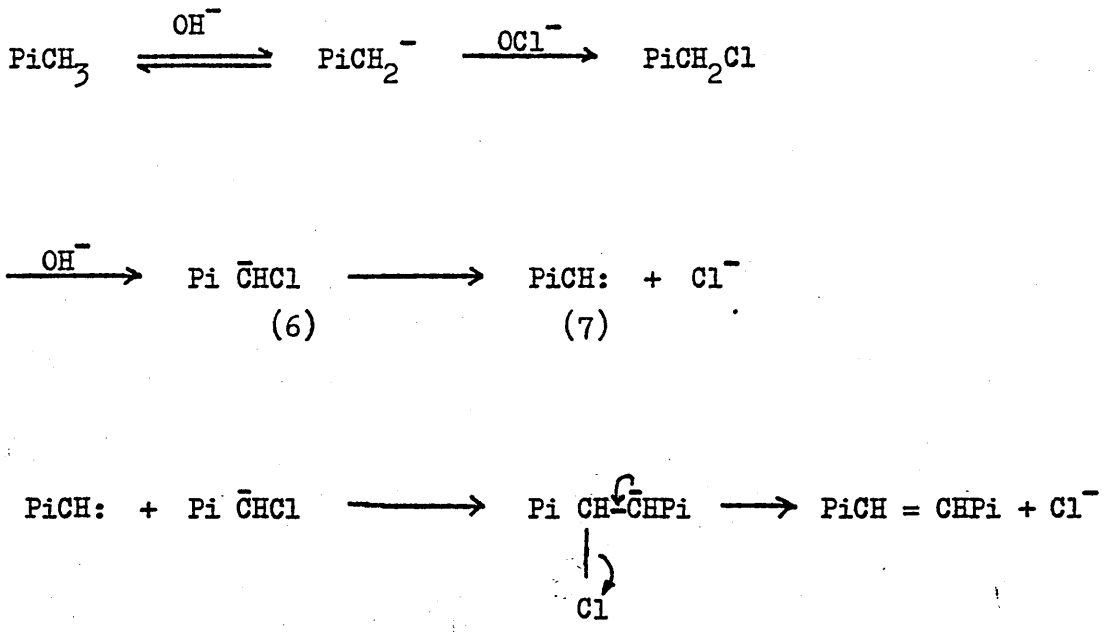
1.2.1 The Shipp Reaction

Shipp and Kaplan achieved the synthesis of HNS by the reaction of TNT in tetrahydrofuran-methanol solution with aqueous sodium hypochlorite[16] (eqn 8).

$$PiCH_3 \xrightarrow{OH^-/OCl^-} PiCH = CH\ Pi \qquad \text{(eqn 8)}$$

This reaction is the basis of the present method for the large scale production of HNS.

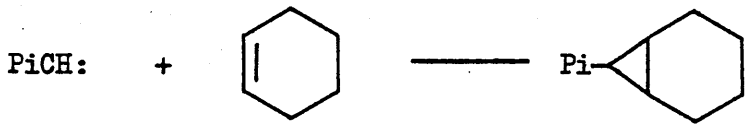
Two mechanisms were considered to explain the formation of HNS. The first involves a carbene (7) as intermediate in the reaction (eqn 9).



(eqn 9)

This idea was tested in an experiment involving the addition of cyclohexene, a carbene trap, to the reaction mixture.

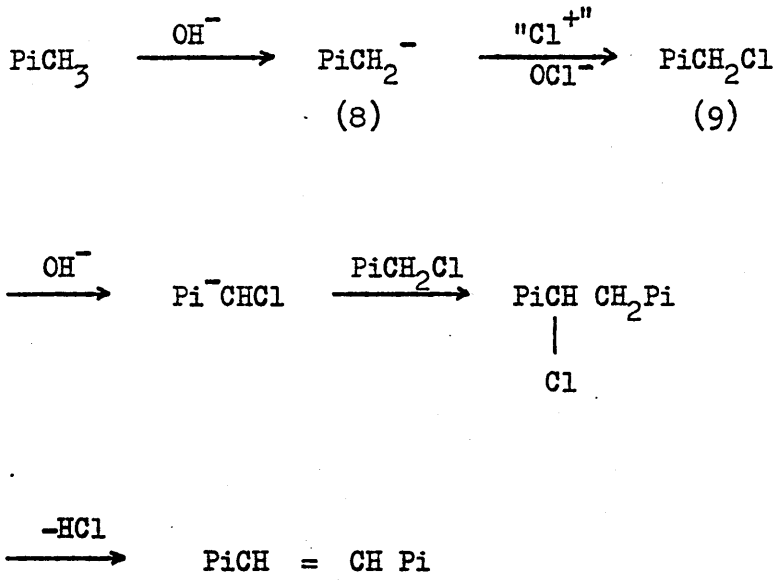
None of the expected product, 7-(2,4,6-trinitrophenyl) norcarane (7a) was obtained. Furthermore, the addition of a large excess of chloride ion, which should increase the return of



(7a)

trinitrophenylmethylene (7) to α-chlorotrinitrobenzyl anion (6) thus reducing the rate of formation of HNS, had little effect.

The second proposal was a displacement-elimination mechanism (eqn 10).



(eqn 10)

The evidence for this mechanism was that 2,4,6-trinitrobenzyl carbanion (8) could be trapped as 2,4,6-trinitrobenzyl chloride (9) by short-stopping the reaction and that changing the mole ratio of alkali to trinitrobenzyl chloride had a pronounced effect on the yield of HNS. The absolute yield of HNS was found to be proportional to the mole ratio of alkali to chloride up to 1 mole of alkali/mole of chloride. As the ratio was increased from unity the yield of HNS decreased until it was negligible at a ratio of alkali to chloride of 2.

It was argued that if trinitrophenylmethylene (7) was an intermediate (eqn 9), increasing the concentration of alkali would favour both its formation and subsequent reaction by increasing the concentration of α-chlorotrinitrobenzyl anion (6). But if a displacement-elimination mechanism was operating, reducing the concentration of unionised trinitrobenzyl chloride in this way, along with side reactions which appeared to irreversibly remove trinitro-

benzyl chloride from the system, would reduce the yield of HNS.

HNBB is a major impurity in HNS prepared by the Shipp method. The reaction can be modified to give good yields of HNBB. A third mechanism proposing the formation of HNS and HNBB by radical intermediates (eqn 11) was discussed.

$$Pi^{-}CHCl + PiCH_2Cl \longrightarrow Pi\dot{C}HCl + PiCH_2Cl^{-\cdot}$$

$$Pi\ CH_2Cl^{-\cdot} \longrightarrow PiCH_2\cdot + Cl^{-}$$

$$2\ PiCH_2\cdot \longrightarrow PiCH_2CH_2Pi$$

$$PiCH_2\cdot + Pi\dot{C}HCl \longrightarrow PiCH_2\underset{\displaystyle Cl}{\underset{|}{C}}H\ Pi \longrightarrow PiCH = CH\ Pi$$

(eqn 11)

This mechanism was not considered likely because it was reported that the TNT anion did not transfer an electron to oxygen to yield the trinitrobenzyl radical under conditions where 4-nitrobenzyl anion readily formed 4-nitrobenzyl radical, which subsequently dimerised to 4,4' - dinitrobibenzyl.

The Shipp method for large scale production of HNS is not without problems. The yield of HNS is low, between 30-40% of the theoretical yield. There are filtration and other procedural difficulties, as well as problems with poisonous, volatile by-products such as trichloronitro-

methane. For these reasons there is a continuing interest in other routes to the synthesis of HNS.

1.2.2 The Hungarian Reaction

In 1975 a Hungarian patent was published which claimed a new method for the synthesis of HNS[17].

TNT was dissolved in a polar aprotic solvent containing a suitable catalyst and an alcoholic solution of potassium hydroxide added dropwise while air was bubbled through the mixture. A buffer solution was added to the mixture which was then warmed for a short time. HNS was precipitated on adding an aqueous solution of a carboxylic acid.

HNBB was the product if the buffer was omitted and the mixture not warmed (eqn 12).

$$PiCH_3 \xrightarrow[\text{catalyst}]{OH^-/O_2} PiCH_2\ CH_2Pi \xrightarrow[\text{warm}]{\text{buffer}} PiCH = CH\ Pi$$

(eqn 12)

The patent contains several examples of the method using a range of polar aprotic solvents. Only two catalysts were used, Siccol NCo 6 (cobalt naphthenate) and a slurry of anhydrous copper sulphate and pyridine.

The patent represented the first published report of the synthesis of HNS by oxidation of TNT or HNBB in basic solution. The preparation of HNBB by oxidation of TNT in basic solution had been reported by Shipp and co-workers, in 1972[69]. They described the use of the trinitrobenzyl anion as a nucleophile in displacement reactions at aromatic carbon to prepare a series of polynitrodiphenylmethanes (eqn 13).

$$PiCH_2^- + Ar\text{-}X \longrightarrow Ar - CH_2Pi + X^-$$

(eqn 13)

It was noticed that in the absence of aryl halide a 41% yield of HNBB was obtained. Formation of HNBB was said to come from the reaction of the trinitrobenzyl anion with TNT (eqn 14).

$$PiCH_2^- + PiCH_3 \longrightarrow PiCH_2CH_2Pi$$

(eqn 14)

The mechanism of the reaction was thought to involve radical ion intermediates in a way similar to that suggested for the formation of 4,4' - dinitrobibenzyl from 4-nitrotoluene in alkaline media[13]. No evidence was presented to support this idea.

1.3 Objectives

HNS is a compound important for its use as a heat-resistant explosive and its apparent unique ability to improve the properties of explosive charges prepared from molten TNT.

As a heat-resistant explosive HNS has the necessary properties of a low vapour pressure and the ability to function satisfactorily at high temperature. Because the need for this type of explosive is on the kilogram rather than tonne scale, a complex synthetic route can be contemplated for manufacture.

On the other hand, because of the vast amount of explosives likely to be used in a war, only a cheap, straightforward method of manufacture

will be useful if HNS is to find widespread use as an additive to TNT charges.

An understanding of the chemistry of HNS will help to identify the most suitable method for its manufacture and it was with this general aim that this research was begun. Of particular interest was the synthesis of HNS by catalytic oxidation of TNT, as outlined in the Hungarian Patent.

The aims of this work were to identify the important parameters affecting this type of reaction, to characterise the products formed and obtain knowledge of their stability under the reaction conditions, and to gain an understanding of the mechanism of the reaction and the intermediates involved.

In the following chapter the literature on the reactions of TNT, HNBB and HNS in basic solution is reviewed. Results are then presented and discussed from experiments in which visible and ^{1}HNMR spectroscopy, in conjunction with electrochemistry and hydrogen-deuterium exchange, have been used to make further contributions to knowledge of the chemistry of these polynitroaromatic compounds.

Chapter 3 goes on to consider the important parameters in the oxidation of TNT to HNBB and HNS. Experimental results are discussed in the light of what is known about the reaction of molecular oxygen with organic compounds and catalysis of such reactions. Possible mechanisms for the formation of HNBB and HNS are considered.

Chapter 4 gives the details of the experiments carried out. The conclusions from this work are contained in Chapter 5.

2. REACTIONS OF POLYNITROAROMATIC COMPOUNDS WITH BASES

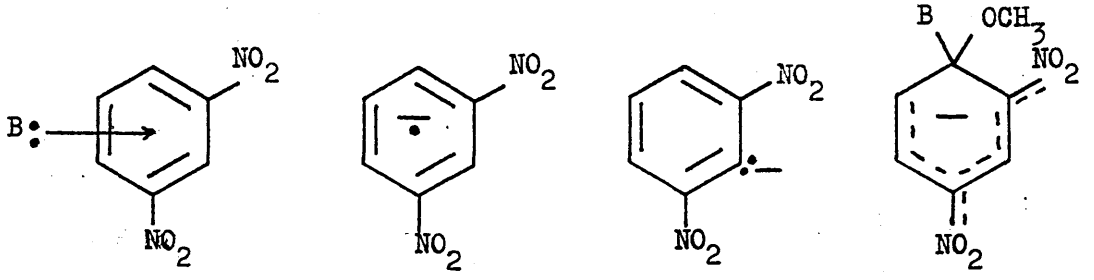
Both the Shipp and Hungarian patent methods for the synthesis of HNS involve reactions of TNT in basic solution. This chapter is concerned with the extent to which the reactions of TNT, HNBB and HNS in basic solution are understood. The present state of knowledge is reviewed, after which the contributions to the subject from this research programme are presented and discussed.

2.1 Introduction

Nitroaromatic compounds produce intense colours in basic solution, the nature of which has been investigated for many years and has been the subject of several reviews.[18,19,20]

Several kinds of interaction between nitroaromatic compounds and bases have now been recognised:

(1) (2) (3) (4)



Charge-transfer complexes (1) arise when the aromatic nucleus, depleted of π-electron density by the electronegative nitro-substituents, accepts electronic charge from a base (B:). In some cases an electron from a base becomes completely transferred to the nitro compound to give a radical anion (2).

If the nitroaromatic compound contains suitably acidic hydrogen atoms proton abstraction may take place to yield a carbanion (3). Alternatively, a covalent bond may be formed between the base and an aromatic carbon atom resulting in the formation of a σ-complex (4). If the compound contains a good leaving group then reaction with base

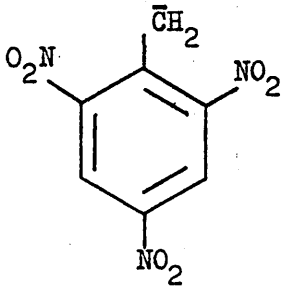
may lead to nucleophilic substitution.

2.2 The Reactions of TNT with Base

The TNT-base system is one where charge-transfer and σ-complexes, radical ions and carbanions are all possible. A considerable amount of work has been undertaken to try and identify, unambiguously, the species involved.

2.2.1 Carbanions

The reaction between TNT and ethoxide ion in ethanol gave a purple species with absorption maxima at approximately 370, 520 and 630 nm[21]. It was concluded that the purple species was the trinitrobenzyl anion (TNT^-, 5).



(5)

Hydrogen-deuterium exchange experiments produced conflicting results. Negligible exchange was observed from TNT in basic 90/10 deuterium oxide-dimethyl sulphoxide[22] and only 23% exchange was observed after several weeks in pyridine-deuterium oxide[23]. However, ready hydrogen-deuterium exchange was observed in basic 10/90 deuterium oxide-dimethylformamide[24].

Some explanation for these conflicting results was given by a temperature-jump study of the reaction of TNT with lyate ions in methanol, ethanol and mixtures of dioxane-water[25]. In the alcohols and 50/50 dioxane-water, with base in excess over TNT, formation of TNT^- was the principal process. But in 10/90 dioxane-water none was detectable.

Thus, in water rich solutions, TNT^- would not be the major species present and exchange would not occur. Only slow exchange was observed in pyridine-deuterium oxide because pyridine is a weak base and only a small amount of TNT^- was formed.

Kinetic studies of the reaction of TNT with alkoxide ion in the corresponding alcohol using stopped-flow apparatus, revealed a large primary isotope effect, around 7, for formation of the purple species[26,27,28]. Results in accord with abstraction of a proton from the methyl group of TNT to give TNT^-.

An NMR investigation of the TNT-base system failed when the spectrum disappeared on adding base to a solution of TNT[29]. But it was predicted that TNT would not be acidic enough to suffer proton loss to methoxide ion but instead would undergo addition at the 3-position. The early NMR problems were overcome by using a flow NMR system. The reaction of TNT with methoxide ion in dimethyl sulphoxide-methanol mixtures was investigated with such a system and the results compared with those from a flow uv-visible study under similar conditions[30]. All the results were consistent with the purple species being the TNT anion.

The pKa of TNT has been measured in ethylene diamine-water mixtures using the Hammett acidity function, H_-[31]. The acidity function is a measure of the ability of a medium to remove a proton, under equilibrium conditions, from weak acids. The amount of ionisation of TNT was measured spectrophotometrically. In this solvent the TNT anion has λmax at 515 nm. At high ethylene diamine concentrations a different spectrum was formed with λmax at 470 and 530 nm. This was assumed to be the TNT dianion.

The first acidity constant $pKa^1 = 14.45$ and the second $pKa^2 = 17.55$.

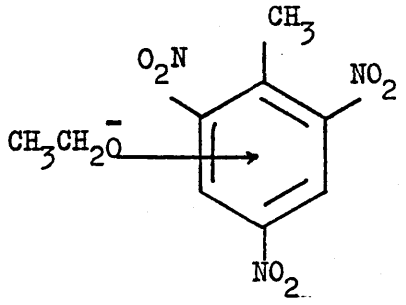
The acidity of TNT in methoxide-methanol mixtures has also been measured[32]. Again a spectrophotometric method was used where the TNT

anion had λmax 520 nm. The acidity constant was pKa^{CH_3OH} = 16.07. The difference between the results from the aqueous system and methanol reflect the different solvation of the ions and neutral molecules in the different solvents.

2.2.2 σ-Complexes

σ-Complexes can be divided into two types. Those in which the attacking base is a carbon base, such as acetonate anion, are known as Janovsky complexes. Complexes with other bases such as methoxide ion, are known as Meisenheimer complexes. Both types of complex can be formed from TNT in basic solution.

During the investigation of the purple species produced from the reaction between TNT and ethoxide ion in ethanol, it was noticed that in concentrated solution, it was possible to detect an initial reaction which rapidly produced a brown solution, which slowly converted to the usual purple[21]. After further investigation it was proposed that this brown species was a charge transfer complex of TNT and ethoxide ion (6)[33].

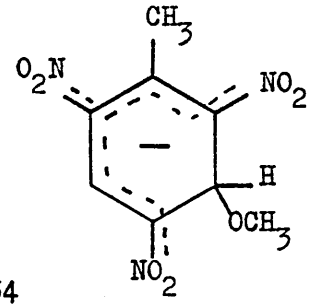


(6)

This initial fast reaction to yield the brown species was noticed by others studying the TNT-base system but it was felt more likely to be a σ-complex of TNT than a charge-transfer complex[25,26].

A study which combined flow NMR and uv-visible spectroscopy showed that in solutions of high dimethyl sulphoxide content and a 1:1 ratio of TNT-methoxide ion, a Meisenheimer complex formed, which then decayed with the formation of TNT^- [30]. In this complex, methoxide ion became

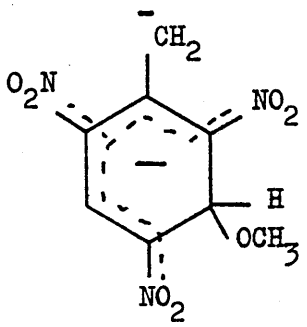
attached at the 3-position (7). Rate and equilibrium data for the formation



(7)

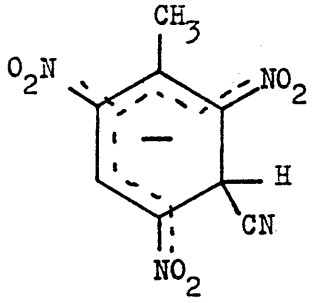
of (7) have been reported[34].

It was also shown that at a 1:2 or lower ratio of TNT-methoxide ion, a dianion formed, in which there was addition of base at the 3-position on the ring and proton abstraction from the methyl group (8).



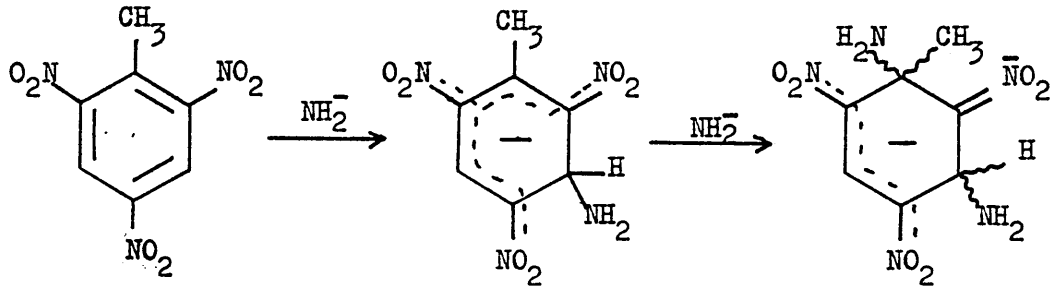
(8)

Other spectral studies have shown that cyanide ion also forms a 3-σ-complex with TNT (9)[35].



(9)

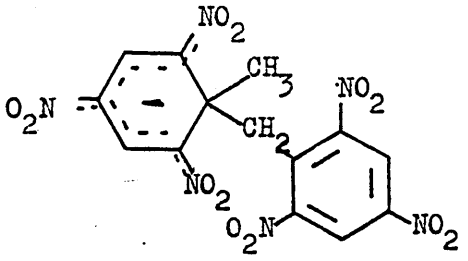
An NMR study of the products formed by dissolving TNT in liquid ammonia, showed that initially a σ-complex was formed by attack of amide ion at the 3-position of the aromatic ring[36]. The spectrum changed with time due to attack by a second amide ion, to give a product which exhibited geometrical isomerism (eqn 1).



(eqn 1)

There was no evidence for the formation of TNT^-.

There is uv-visible spectral evidence that when TNT was in excess over base, formation of a Janovsky complex between TNT^- and a second molecule of TNT was possible (10)[25].



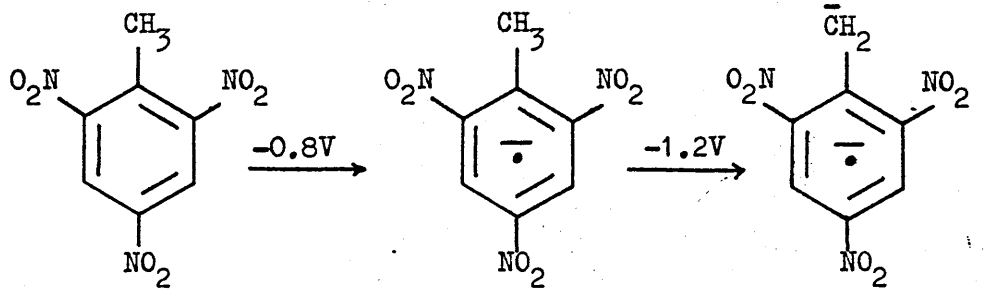
(10)

In aqueous solution in the presence of surfactant, TNT reacted with bases to give a σ-adduct which, from the evidence, was also thought to be a Janovsky complex (10)[37]

2.2.3 Radical Species

Information on whether TNT forms radicals in basic solution is confused. No radicals were reported from TNT in t-butanol in the presence of excess t-butoxide ion[38]. Weak ESR signals were detected from TNT in dimethyl sulphoxide-t-butanol (4:1) in the presence of base but it was thought this might be due to oxidation of the solvent, catalysed by the nitro-compound. A later paper repeated that TNT did not produce radical species in the presence of a deficiency of base but the solvent used was not clear[39]. Early attempts to measure the ^{1}HNMR of TNT in basic solution were foiled by the complete disappearance of the spectrum, which hinted at the presence of paramagnetic species[29]. The problem was solved by using a flowing system. When this system was adapted to an ESR spectrometer, very large quantities of radicals were found from the reaction of TNT with methoxide ion in 87.5% dimethyl-sulphoxide - 12.5% methanol[30]. What is more, the rate of disappearance of the radicals was similar to that of the disappearance of the TNT anion under similar conditions.

Electrolytic reduction of TNT in DMF, DMSO and acetonitrile produced a radical species whose ESR spectrum was consistent with that of the TNT radical anion ($TNT^{\cdot -}$, 11)[40]. At more negative potentials a new spectrum appeared, which was interpreted as the dinegative trinitrobenzyl radical (12), resulting from elimination of a methyl proton from $TNT^{\cdot -}$.



(11) (12)

2.3 The Reactions of HNBB and HNS with Base

There is very little information in the literature on the reactions of base with HNBB and HNS. The reaction between ethylenediamine (EDA) and HNBB and HNS was investigated as a possible method of assaying the compounds[41]. The red-brown solutions produced had two maxima in their visible spectra. HNBB, 465 nm ($E = 6.25 \times 10^4 dm^3.mol^{-1}.cm^{-1}$) and 530 nm ($E = 3.10 \times 10^4 dm^3.mol^{-1}\ cm^{-1}$); HNS, 460 nm ($E = 6.45 \times 10^4 dm^3.mol^{-1}\ cm^{-1}$) an 510 ($E = 3.39 \times 10^4 dm^3.mol^{-1} cm^{-1}$). The products responsible for these spectra were thought to be Meisenheimer adducts.

Base catalysed dehydrogenation of HNBB by quinones yielded HNS[42]. The mechanism proposed for this reaction involved the carbanion of HNBB which, it was claimed, showed absorption maxima at 460 and 500 nm in basic ethanol.

In summary, there is good evidence that the major reaction of TNT in basic alcohol or DMSO/alcohol solutions was ionisation to yield the trinitrobenzyl anion, TNT^-. In the early stages of the reaction σ-complex formation occurs in which base becomes attached at the 3-

position of the aromatic ring.

With excess base in DMSO-methanol solution, a dianion could be formed, in which there was addition of base at the 3-position on the ring and proton abstraction from the methyl group. When TNT was in excess over base, formation of a Janovsky type of σ-complex between TNT^- and a second molecule of TNT was possible.

When TNT was dissolved in liquid ammonia there was no evidence for the formation of TNT^-. Initially a σ-complex was formed by attack of amide ion at the 3-position of the aromatic ring, later attack by a second amide ion at the 1-position, gave a product which showed geometrical isomerism.

There is also strong evidence for the formation of radicals from TNT in basic solution. TNT radical anions can be generated electrolytically in polar aprotic solvents but the nature of the radicals produced in basic solution is not clear.

The literature contains little information about reaction of HNBB and HNS with base. There is some evidence for the formation of σ-complexes between EDA and HNBB and HNS and tentative spectroscopic evidence for the formation of the carbanion of HNBB in basic ethanol.

The aim of the work which follows was to compare and contrast the behaviour of TNT in the basic media used in the formation of HNS, with the results published in the literature and to contribute to knowledge of the chemistry of HNBB and HNS in basic solution. This information will ultimately be useful in understanding the mechanism of the oxidative coupling reaction of TNT to HNBB and HNS.

2.4 Experimental Results and Discussion

The reactions of TNT, HNBB and HNS in basic solution, have been studied by visible and ^{1}HNMR spectroscopy, hydrogen-deuterium exchange experiments and electrochemical methods. Spectroscopy has been used in conjunction with information from the literature, to investigate which of the many possible intermediates were present in basic solutions of the nitroaromatic compounds. Exchange experiments can establish whether ionisation of a methylene proton of HNBB is a major pathway in its reaction with base. The importance of radicals in these systems was investigated by generating them electrolytically from solutions of the nitroaromatic compounds in aprotic media. The spectral characteristics of the solutions were established and these results compared with those from reaction mixtures.

2.4.1 Visible Spectroscopy

Solutions of TNT, HNBB and HNS, in common with many other nitro compounds, produce intense colours in the presence of base. The Hungarian Patent method of oxidative coupling of TNT in basic solution to HNBB and then HNS, illustrated the sorts of colours produced.

A transient brown colour was first observed on mixing TNT and base solutions. During the first minute after mixing, this brown colour gave way to purple. Five minutes after mixing, the purple colour began to be replaced by a red-brown which intensified over the next twenty minutes. Warming the mixture to 55°C at this point changed its colour from red-brown to blue.

There is now considerable information on the spectral characteristics of some of the species produced by the interaction of nitroaromatic compounds with base[18,19,20]. Such information has been used below to identify the species responsible for some of the colours seen during the oxidative coupling of TNT by the Hungarian Patent method.

The Nature of the Brown Colour

The brown colour appeared and disappeared too quickly for its visible spectrum to be obtained with a conventional spectrometer. However, an initial fast reaction to form a brown species has been reported by others studying the TNT-base system and has been studied by more sophisticated techniques.

The brown colour was first thought to be due to a charge-transfer complex of TNT and base[33]. But when TNT, deuterated in the methyl group, was reacted with sodium isopropoxide in isopropanol at about -60°C, it was possible to obtain a visible spectrum of the brown species[27]. The spectrum had absorption maxima at 435 and 495 nm. The wavelengths of the maxima, as well as the values of the extinction coefficients, were characteristic of σ-complexes in the trinitrobenzene series, where such complexes could be identified unambiguously by NMR.

A similar spectrum was obtained from TNT with methoxide ion in DMSO-methanol solution (λ max 433, 505 nm), using a flowing system in which the early stages of the reaction could be easily studied. A flow-NMR investigation of the same reaction confirmed the brown species to be a σ-complex and furthermore, showed that there had been addition of base at the 3-position of the aromatic ring[30]. There have been no definite examples of addition of base at the 1-position of the TNT aromatic ring, although the visible spectra of 1- and 3-σ-complexes of trinitro-compounds are similar. The electron donating inductive effect of the methyl group makes the 1-position less susceptible to attack than the 3-position.

In the light of the above information it was reasonable to assign the brown colour seen in the early stages of the oxidative coupling reaction of TNT, to a 3-σ-complex of TNT and base.

The Nature of the Purple Colour

The visible spectrum of the purple solution is shown in Fig. 2.1.A. The spectrum had absorption maxima at 380 nm, 520 nm and a broad shoulder centred around 620 nm. A similar spectrum was obtained from a solution of TNT (7.6×10^{-5} mol.dm^{-3}) in 90/10 DMF-methanol, in the presence of a large excess of potassium hydroxide (3.9×10^{-2} mol.dm^{-3}).

Assuming that, in the presence of such a large excess of base, all of the TNT had reacted, then the extinction coefficients for the purple species can be calculated as:-

λ max/nm	E/dm^3.mol^{-1}.cm^{-1}
380	7.5×10^3
520	1.5×10^4
620	5.0×10^3

The wavelengths of the absorption maxima and the values of the extinction coefficients were typical of TNT^- [26,30].

Thus, this suggests that, under the specified conditions, the oxidative coupling reaction of TNT involves the fast formation of a 3-σ-complex and the subsequent, slower formation of TNT^-.

The Nature of the Red-Brown Colour

The visible spectrum of the reaction mixture when it was red-brown in colour is shown in Fig. 2.1.B. The spectrum had two absorption maxima, at 444 nm and 500 nm, with the extinction coefficient of the shorter wavelength maximum about 1.5 times greater than that of the longer wavelength maximum.

Of the different products that can be formed by the interaction of nitroaromatic compounds with base, σ-complexes have received the most thorough investigation. This is because of the information they provide on the mechanism of aromatic nucleophilic substitution reactions. A

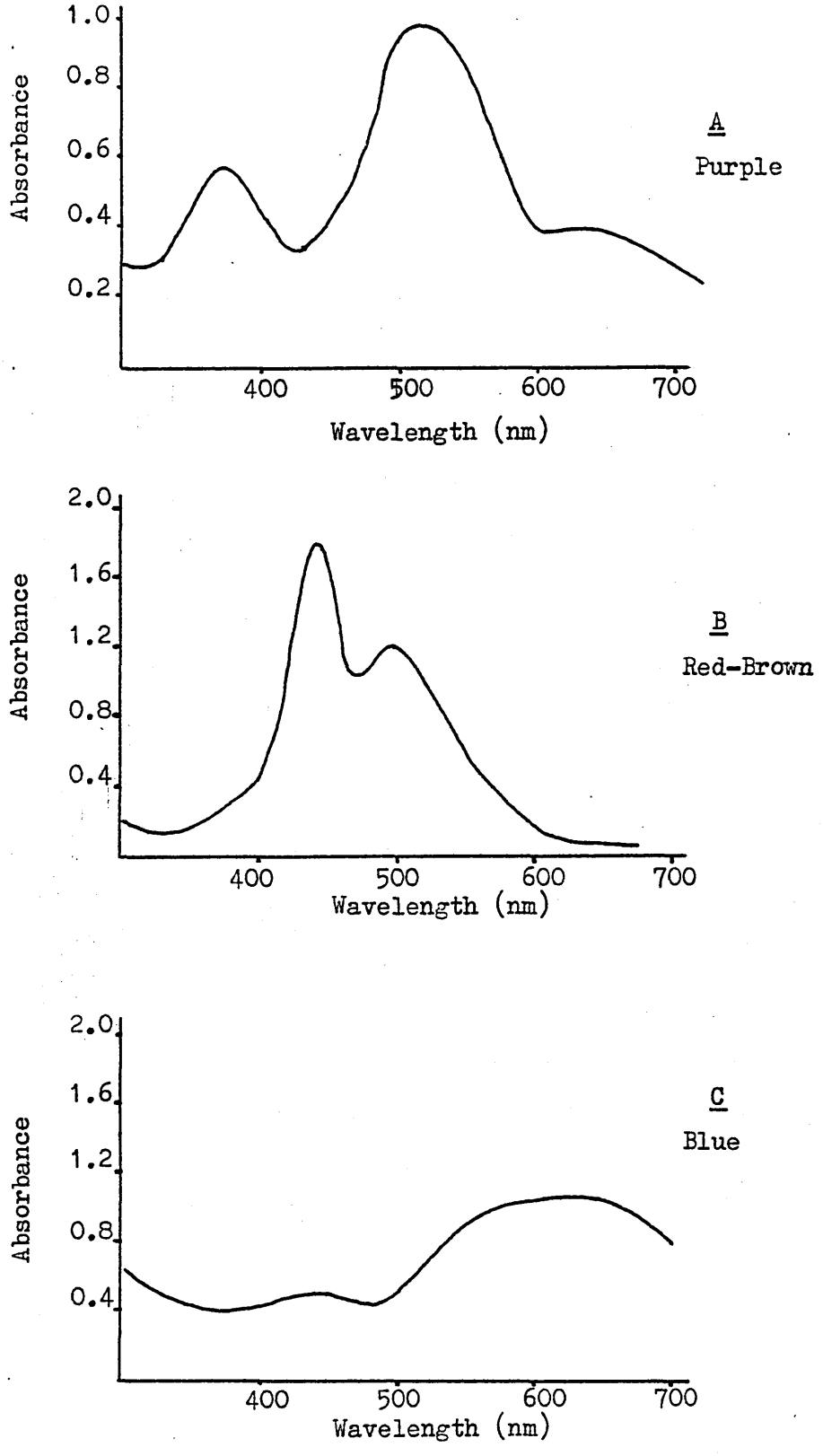


Fig. 2.1 Visible spectra from a solution of TNT (2×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol in the presence of potassium hydroxide (2×10^{-1} mol.dm.$^{-3}$).

great deal of information is now available on the spectral characteristics of σ-complexes formed from 2,4,6 - trinitroaromatic compounds with base.

Almost all of the spectra of such complexes display two distinct maxima in the visible region of the spectrum. The molar extinction coefficient of the high-energy band is typically a factor of 1.3 to 2.5 times larger than the low-energy band and has a value in the range $2.4 \times 10^4 dm^3.mol^{-1}.cm^{-1}$ [18]. The spectrum in Fig. 2.1.B. shows all the characteristics expected from a σ-complex.

If the reaction was stopped when the red-brown colour had become well established, the predominant product was HNBB. This strongly suggested that the red-brown colour was due to a σ-complex formed by reaction of HNBB with base. Indeed, a spectrum similar to Fig. 2.1.B. was obtained from the reaction of HNBB (3.8×10^{-5} mol.dm^{-3}) with excess potassium hydroxide (2×10^{-2} mol.dm^{-3}) in 90/10 DMF-methanol. Extinction coefficients, calculated by assuming that in the presence of such a large excess of base, all of the HNBB had reacted, are:-

λmax/nm	$E/dm^3.mol^{-1}.cm^{-1}$
444	5.4×10^4
494	3.9×10^4

The slight difference in position of the longer wavelength maximum in the spectrum of the original reaction mixture, Fig. 2.1.B., reflected a contribution to that spectrum from residual TNT^-.

The magnitude of the extinction coefficients was higher than the typical value for trinitroaromatic compounds. For example, the σ-complex from interaction between TNT and methoxide ion in DMSO-methanol, had an extinction coefficient of $1.8 \times 10^4 dm^3.mol^{-1}.cm^{-1}$ for its high energy maximum[30]. The higher value for extinction coefficients from HNBB under similar conditions suggested that reaction with both aromatic rings occurred.

The only other reported example of σ-complex formation from interaction between HNBB and base was with ethylenediamine in DMSO[41]. The visible spectrum of this complex had absorption maxima at:-

λ max/nm	$E/dm^3.mol^{-1}cm^{-1}$
465	6.25×10^4
530	3.10×10^4

The shift to longer wavelengths of the absorption maxima compared to HNBB/potassium hydroxide/DMF-methanol system, was due to both the different solvent and the different nucleophile involved.

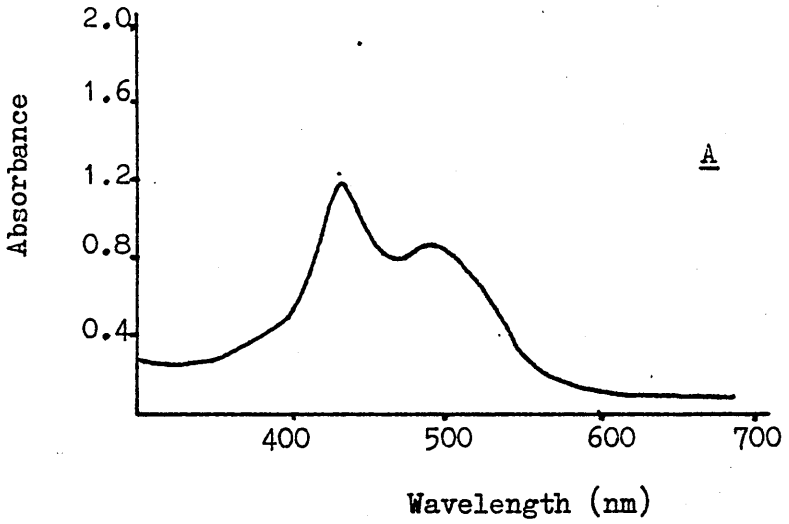
The red-brown colour observed during the oxidation of TNT was thus assigned to a σ-complex of HNBB, on the basis of the similarity of its visible spectrum with those of well-established σ-complexes of trinitro-aromatic compounds.

The Nature of the Blue Colour

The visible spectrum of the blue colour which characterised the reaction mixture in its later stages, is shown in Fig. 2.1.C. The major feature of the spectrum was the broad absorption maximum centred around 610 nm. If the reaction was stopped when the blue colour was well established the predominant product was HNS.

The origin of the blue colour might lie in some interaction between base and HNS, as it was produced. In the same way that HNBB, formed from oxidation of TNT, immediately reacted with base to yield a σ-complex. Alternatively, the colour might come from some intermediate or by-product involved in the dehydrogenation of HNBB to HNS. These ideas were tested by trying to generate the blue colour, first from solutions of HNS in the presence of base, then secondly from basic solutions of HNBB.

The visible spectrum of a solution of HNS (2.8×10^{-5} mol.$dm.^{-3}$) in 90/10 DMF-methanol, in the presence of potassium hydroxide (3.9×10^{-2} mol. $dm.^{-3}$), Fig. 2.2.A, had all the characteristics of that of a σ-complex:



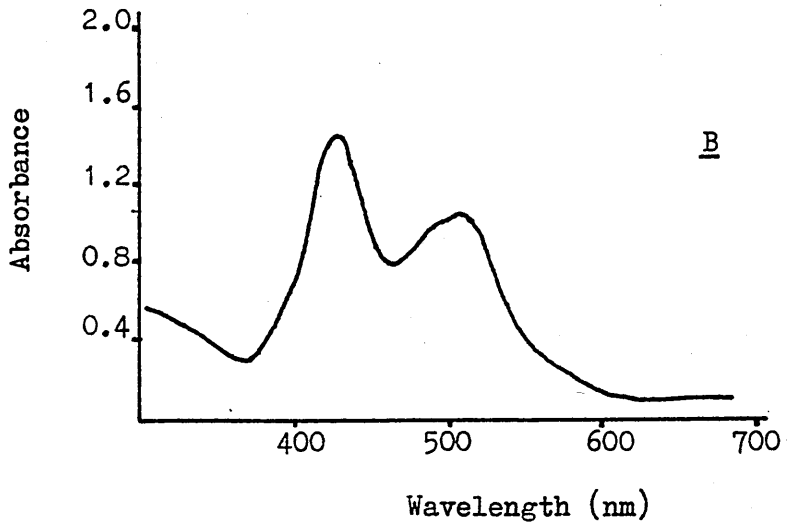


Fig. 2.2 A. Visible spectrum from a solution of HNS (2.8×10^{-5} mol.dm.$^{-3}$) in 90/10 DMF-methanol in the presence of potassium hydroxide (3.9×10^{-1} mol.dm.$^{-3}$).

B. Visible spectrum of a diluted sample from a reaction mixture of HNS and potassium hydroxide (both 2×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol.

λ max/nm	$E/dm^3.mol.^{-1}cm.^{-1}$
438	4.2×10^4
486	3.1×10^4

At the higher concentrations used in preparative work, around 2×10^{-1} mol.dm.$^{-3}$, the reaction between equimolar HNS and potassium hydroxide gave a red-brown solution, with a visible spectrum of similar shape to that obtained at lower concentrations but with different wavelengths for the absorption maxima, Fig. 2.2.B. The spectrum had maxima at 430 and 512 nm with a shoulder around 490 nm. The spectrum remained stable for over 60 min.

The results suggested that HNS readily formed a stable σ-complex on interaction with base and that reaction between base and HNS as it was formed, was not the cause of the blue colour.

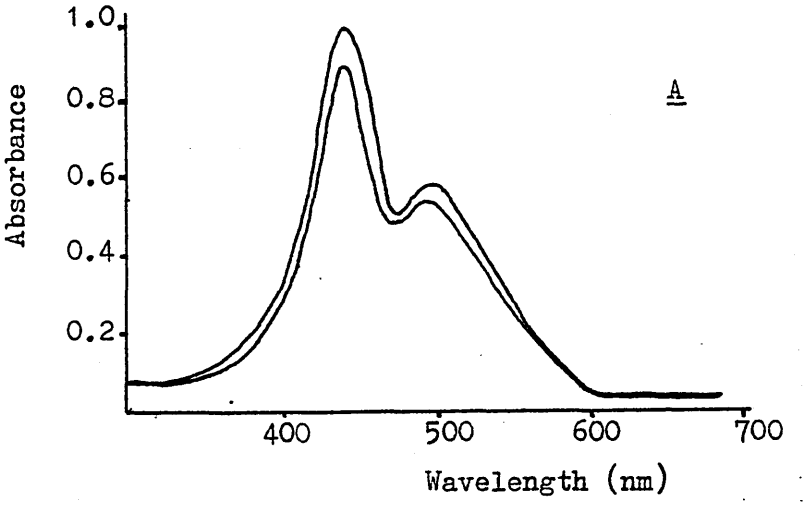
Warming the reaction mixture to 55°C, promoted the dehydrogenation of HNBB, formed from TNT, to HNS. If the blue colour was from some intermediate or by-product in this dehydrogenation it should be possible to produce it by warming a solution of HNBB.

The visible spectrum of a solution of HNBB (2×10^{-4} mol. dm.$^{-3}$) in the presence of an excess of sodium methoxide, had the typical σ-complex characteristics:

λ max/nm	$E/dm^3.mol.^{-1}cm.^{-1}$
444	5.6×10^4
502	2.9×10^4

Warming this solution to 55°C caused its spectrum to fade slowly over 60 min but there was no increased absorbance above 600 nm, Fig. 2.3.A.

At the higher concentrations encountered in preparative work, a solution of HNBB (1.7×10^{-1} mol.dm.$^{-3}$) and sodium methoxide (1.7×10^{-1} mol.dm.$^{-3}$) in DMSO-methanol, was initially red-brown, with a typical



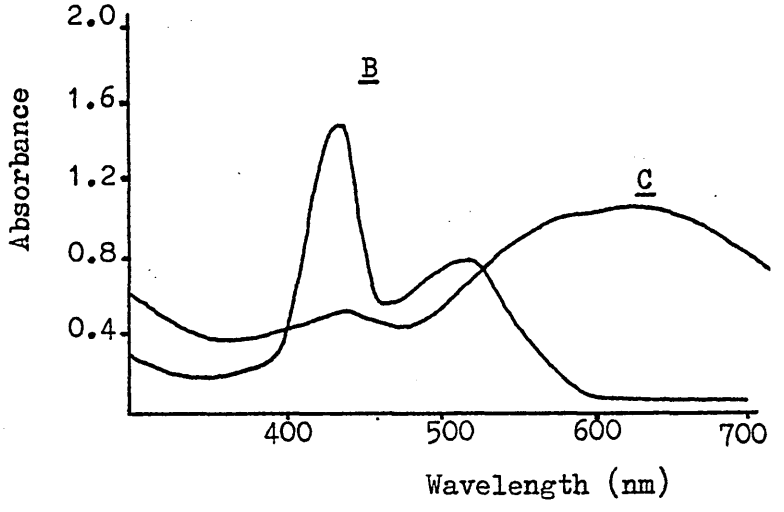


Fig. 2.3.A Visible spectra from a solution of HNBB (2.0×10^{-4} mol.dm.$^{-3}$) in 90/10 DMF-methanol in the presence of sodium methoxide (2.5×10^{-2} mol.dm^{-3}), 55°C, 1 hr. repeat.

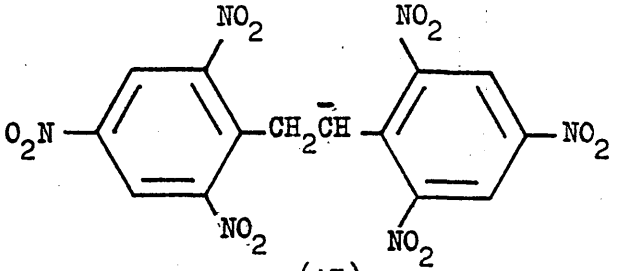
B Visible spectrum from a diluted sample of a solution of HNBB (1.7×10^{-1} mol. dm.$^{-3}$) in 90/10 DMSO-methanol in the presence of sodium methoxide (1.7×10^{-1} mol. dm.$^{-3}$).

C Visible spectrum from a similar sample 90 min. later.

σ-complex spectrum, Fig. 2.3.B. With time, the solution turned dark blue and HNS began to be precipitated. The visible spectrum of the solution at this point, showed a broad absorption around 625 nm, Fig. 2.3.C. Warming the mixture decreased the time before the blue colour became established.

Thus, the blue colour could be produced from basic solutions of HNBB but not HNS. This strongly suggested that the colour arose from some intermediate or by-product involved in the dehydrogenation of HNBB to HNS.

The nature of the visible spectrum of the blue species, Fig. 2.3.C, showed it not to be a σ-complex. An alternative reaction between nitroaromatic compounds and base is proton abstraction, as was seen with TNT. The HNBB anion (13) has been proposed as an intermediate in the dehydrogenation of HNBB by quinones to form HNS.[42]



(13)

These authors claimed, in a footnote, that preliminary spectroscopic evidence was available to show that the carbanion (13) was formed in basic ethanolic solution and that it had absorption maxima at 460 and 500 nm.

The spectrum obtained from a solution of HNBB and sodium ethoxide in ethanol is shown in Fig. 2.4. It has absorption maxima at 440 and 530 nm and closely resembles the spectrum expected for a σ-complex of HNBB and cannot be taken as evidence for the existence of the HNBB carbanion (13).

Very little information is available on the spectral characteristics of carbanions of nitroaromatic compounds. The visible spectrum of TNT^-,

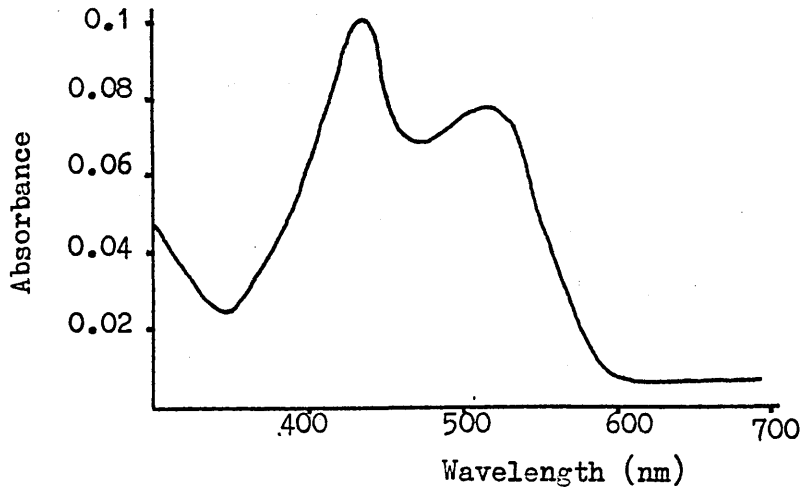
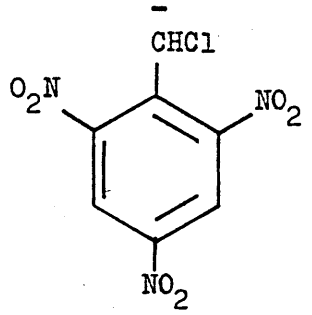


Fig. 2.4 Visible spectrum from a solution of HNBB (6×10^{-6} mol. dm.$^{-3}$) in ethanol in the presence of sodium ethoxide (1×10^{-2} mol. dm.$^{-3}$)

see Fig. 2.1.A, had absorption maxima at around 380, 520 and 620 nm, and the spectrum of the conjugate base of 2,4,6 - trinitrobenzyl chloride (14) was similar[37].



(14, $TNBCl^-$)

The HNBB carbanion (13) is derived from a methyl-substituted TNT derivative in the same way as $TNBCl^-$ (14). Delocalisation of the negative charge can only occur over one aromatic ring in both cases, which suggests the HNBB carbanion (13) will have a similar spectrum to $TNBCl^-$ (14) and TNT^-, Fig. 2.1.A, this was not observed.

In conclusion, the visible spectra recorded at different stages in the conversion of TNT to HNS by the Hungarian Patent method, provided some indication of the nature of the species present in the reaction mixture.

The transient brown colour seen at the start of the reaction was due to a 3- σ-complex of TNT which was quickly converted to the purple trinitrobenzyl anion, TNT^-. The purple colour was then itself replaced by the red-brown of a σ-complex of HNBB. The final stages of the reaction were marked by a blue colour from an intermediate or by-product of the dehydrogenation of HNBB to HNS, of uncertain origin.

2.4.2 ^{1}HNMR Spectroscopy

The most conclusive evidence on the structure of intermediates from the reactions of nitroaromatic compounds with base has come from ^{1}HNMR. The interactions between TNT, HNBB and HNS with base have been

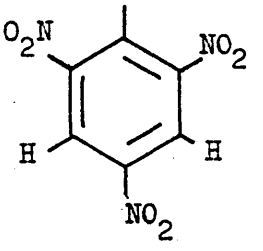
studied by ^{1}HNMR and the results are discussed below. The conditions used in the experiments were kept as close as possible to those used in the oxidation of TNT to HNBB and HNS by the Hungarian Patent method.

TNT

The 60 MHz. ^{1}HNMR spectrum of TNT in DMSO-D_6 showed two singlets:

δ 2.55 ppm 3H $-CH_3$

δ 9.15 ppm 2H



(Fig. 2.5.A.)

The initial spectrum of a solution of TNT (3.2×10^{-1} mol.dm.$^{-3}$) in 80/20 DMSO-D_6/methanol-D_4 in the presence of potassium hydroxide (4×10^{-1} mol.dm.$^{-3}$) showed no signals at all. But at full instrument gain the spectra shown in Fig. 2.5 were recorded. The signals from the aromatic and methyl protons of TNT had disappeared and been replaced by broad signals which changed in intensity over the time period studied.

It had been previously reported that the addition of methoxide ions to a solution of TNT in a variety of solvents, led to complete disappearance of the resonance absorptions of the aromatic protons of TNT[29]. In contrast, the complex formed in deutero-chloroform solution between cyanide ion and TNT was readily examined by ^{1}HNMR[35] and was shown to have a spectrum consistent with a 3- σ-complex, Table 2.1.

The problem of studying the interaction between TNT and methoxide ions was overcome with a system in which spectra were recorded as the reactants flowed through a modified sample cavity[30]. Using this flow

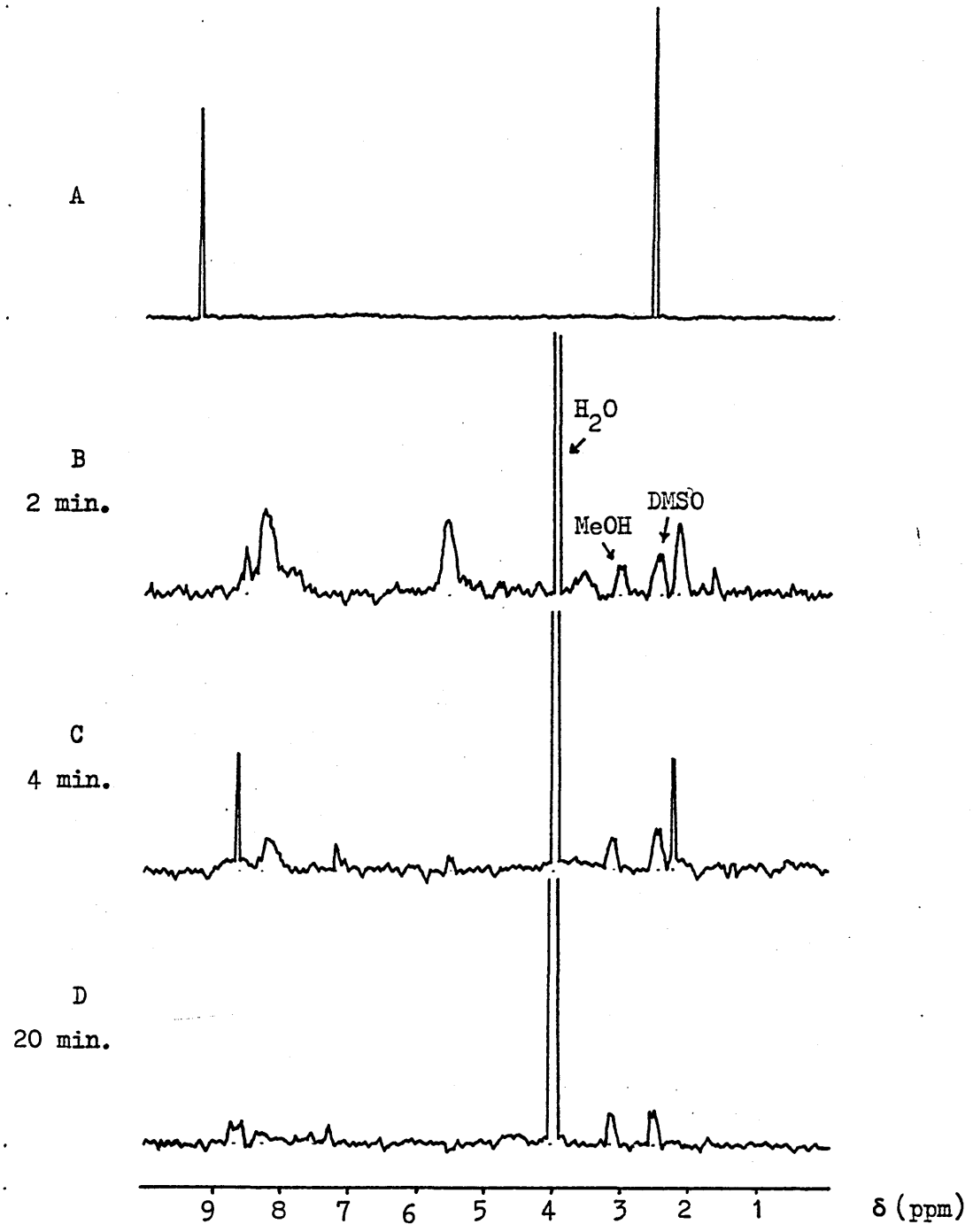


Fig. 2.5 A ^{1}HNMR spectrum of TNT in DMSO-D_6

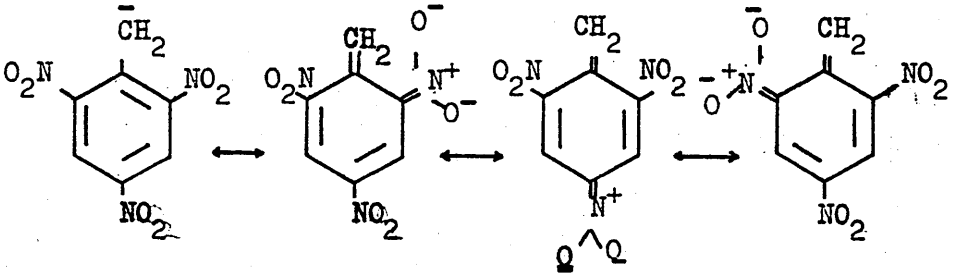
B Spectrum of TNT (3.2×10^{-1} mol.dm.$^{-3}$) in 80/20 DMSO-D_6-methanol-D_4, 2 min. after mixing with potassium hydroxide (4×10^{-1} mol.dm.$^{-3}$)

C Spectrum 4 min. after mixing.

D Spectrum 20 min. after mixing.

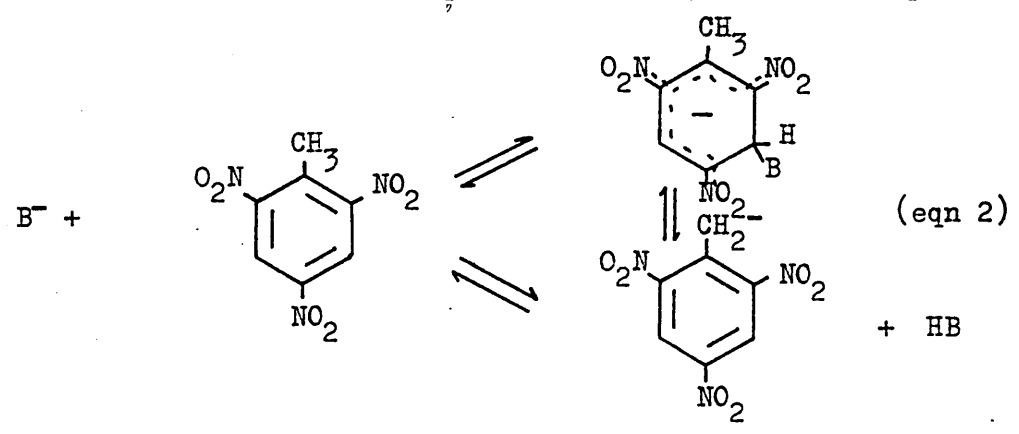
method for ^{1}HNMR and visible spectroscopy, the transient and stable species formed in the reaction of methoxide ions with TNT in DMSO-methanol mixtures were identified. The data recorded in that study, Table 2.1, were used to interpret the spectra in Fig. 2.5.

The signals at δ 8.3 and 5.6 ppm in Fig. 2.5.B, were assigned to the ring protons and methylene group of TNT^-. The negative charge on the methylene group in TNT^- is delocalised over the molecule by resonance:



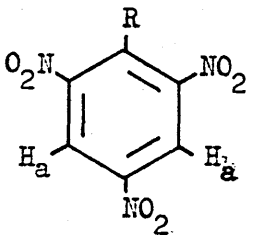
The downfield shift from δ 2.55 ppm in TNT to δ 5.6 ppm on ionisation reflected the change in hybridisation at the substituent carbon atom, from sp^3 to sp^2. The upfield shift in the ring protons signal, from δ 9.15 ppm in TNT to δ 8.3 ppm in the carbanion was due to the increased negative charge on the ring.

The NMR results thus confirmed that, under the specified conditions, the oxidative coupling of TNT involved the formation of TNT^-. The 3- σ -complex, which was observed by more sophisticated experiments, formed and decayed away too quickly to be seen in this experiment. TNT^- could be formed from the 3- σ -complex or directly from TNT (eqn 2).



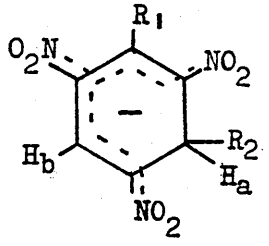
(eqn 2)

Table 2.1 Proton Chemical Shifts of some Polynitroaromatic Compounds and their Products from Reaction with Bases.



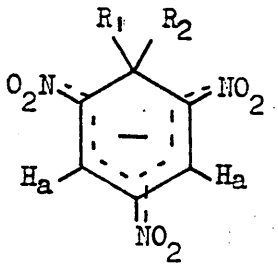
—δ ppm ——————

R	Solvent	Ha	Others		Ref
CH_3	DMSO-D_6	9.15	CH_3	2.55	–
CH_2CH_2Pi	DMSO-D_6	9.1	CH_2CH_2	3.4	–
CHCHPi	DMSO-D_6	9.2	CHCH	7.2	–
CH_2Cl	75/25 DMSO-D_6-methanol-D_4	9.09	CH_2Cl	5.0	37
CH_2Pi	DMSO-D_6	9.06	CH_2Pi	5.12	69
CHO	$CDCl_3$	9.37	CHO	10.73	35
CH_3O	DMSO	9.1	CH_3O	4.1	29

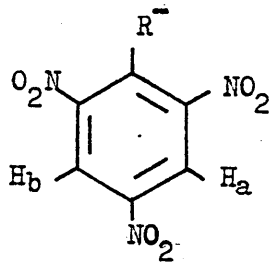


—————— δ ppm ——————

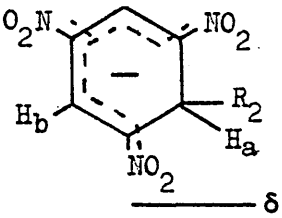
R_1	R_2	Solvent	Ha	H_b	Others		Ref
CH_3	CH_3O	93/7 DMSO-methanol	6.18	8.45	—		30
CH_3	CN	$CDCl_3$	5.76	8.65	CH_3	2.74	35
CH_3	NH_2	NH_3	5.36 (d) ($J_{a,b}$ 1.2 Hz)	8.31 (d)	CH_3	2.23	36



R_1	R_2	Solvent	δ ppm H_a	Others	Ref
CH_2Cl	CH_3O	75/25 DMSO-D_6-methanol-D_4	8.70	CH_2Cl 4.68 CH_3O 3.0	37
CH_3O	CH_3O	DMSO	8.67	CH_3O 3.06	29
CH_3O	$(CH_3CH_2)_2N$	DMSO	8.65	CH_3O 3.08	29
CHO	CN	$CDCl_3$	8.55	CHO 10.14	35



R	Solvent	δ ppm H_a	H_b	Others	Ref
CH_2	93/7 DMSO-methanol	8.18	8.18	CH_2 5.53	30
CHCl	75/25 DMSO-D_6-methanol-D_4	8.20(d)	8.50(d) ($J_{a,b}$ 2.3 Hz)	CHCl 6.90	37
CHPi	DMSO-D_6	8.70	8.70	CHPi 6.92	69



			δ ppm				
R_1	R_2	Solvent	H_a	H_b	Others		Ref
CH_2	CH_3O	93/7 DMSO-methanol	6.18	8.45	CH_2	6.42, 6.52	30
CHCl	CD_3O	75/25 DMSO-D_6 methanol-D_4	6.22(d)	8.68(d) ($J_{a,b}$ 3 Hz)	CHCl	7.55	37

There is, however, some evidence to suggest that the reaction was more complex. The efficiency of conversion of the different species has been measured in basic DMSO-methanol by an NMR experiment using benzene as an internal standard[30]. The efficiency of conversion of TNT to its 3- σ -complex was 95%, but the conversion to TNT^- was only 50%. Furthermore, when conversion to the anion was complete there were no other peaks in the spectrum. This anomaly was explained if neutral species and anion radicals were both produced in the reaction. The anion radicals underwent electron exchange reactions with the neutral species, including TNT, and the NMR spectra of any neutral species were broadened and not observed. The spectra of charged species such as TNT^- were not affected because being negatively charged they were not involved in exchange reactions. The implication of this observation was the existence in such solutions of substantial concentrations of radicals.

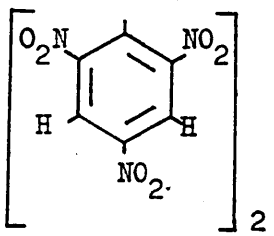
The signals from TNT^- had all but disappeared 4 mins. after mixing the reactants, Fig. 2.5.C. But signals at δ 8.6 and 2.3 ppm had increased in intensity relative to the residual undeuterated solvent peaks at δ 3.1 and 2.5 ppm. Visible spectra of similar solutions of TNT in the presence of base have already shown that TNT^- was soon replaced by a σ-complex of HNBB, see above. Such a complex might give rise to the signals at δ 8.6 and 2.3 ppm. This premise was tested by recording NMR spectra from HNBB in the presence of base.

HNBB

The 60 MHz ^{1}HNMR spectrum of HNBB in DMSO-D_6 showed two singlet absorption resonances:

δ 3.4 4H $-CH_2CH_2-$

δ 9.1 4H

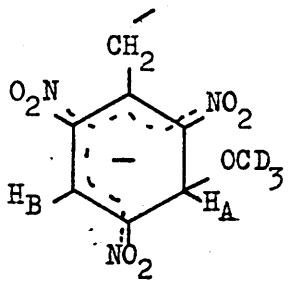


(Fig. 2.6.A.)

A reaction mixture containing HNBB (2.5×10^{-1} mol.dm.$^{-3}$) and sodium methoxide (2.5×10^{-1} mol.dm.$^{-3}$) in 90/10 DMSO-D_6/methanol-D_4 was prepared in an NMR tube and its spectrum recorded at time intervals over 30 min, Fig. 2.6. The signals corresponding to HNBB broadened and other signals appeared. The solution was red-brown at the start of the experiment and dark blue at the finish.

Reactions of HNBB with base have not previously received much investigation. The results from this experiment were compared and contrasted with those from studies of the reactions with base, of TNT and TNBCl, the compounds most similar to HNBB, for which information was available, Table 2.1.

Thus, the signals at δ 8.5 and 6.1 ppm in Fig. 2.6.B., were typical of a σ-complex in which base attack has occurred at the 3-position of an aromatic ring (15).



(15)

The signal at δ 6.1 ppm was due to H_A. The shift upfield from 9.1 ppm in HNBB was due to the change in hybridisation at the 3-ring carbon, from sp^2 to sp^3. The resonance absorption at δ 8.5 ppm was from H_B, shifted upfield from δ 9.1 ppm in HNBB because of the increased negative charge on the aromatic ring in the complex.

What was not obvious in Fig. 2.6.B., was a signal which could be attributed to the methylene group of the 3- σ -complex. Now, in the 3- σ -adduct formed from TNT and cyanide ion[35], the signal due to the methyl group was only slightly shifted from its position in TNT. It moved from δ 2.82 ppm in TNT to δ 2.74 in the adduct. Assuming such a

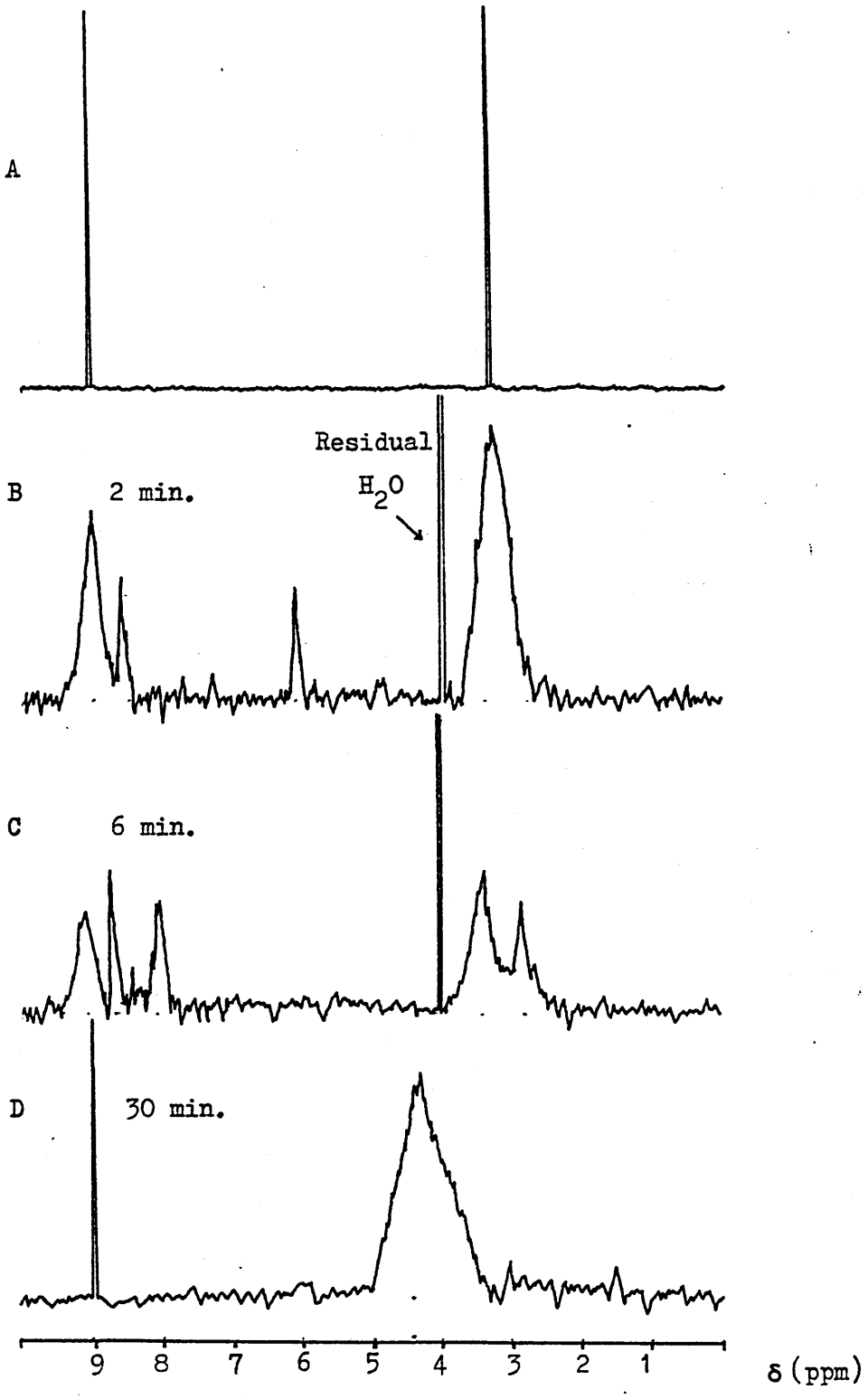


Fig. 2.6. A ^{1}HNMR spectrum of HNBB in DMSO-D_6

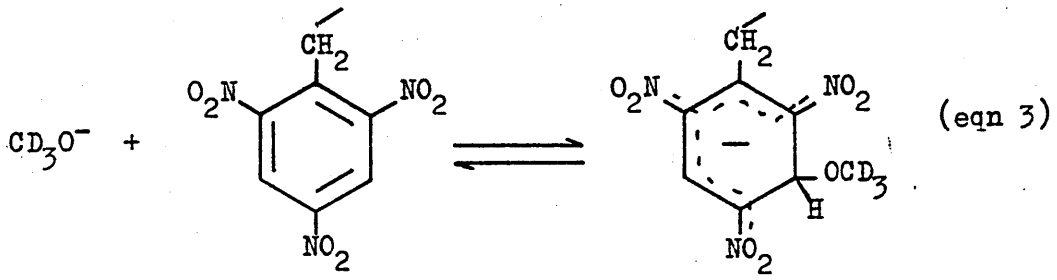
B Spectrum of HNBB (2.5×10^{-1} mol.dm.$^{-3}$) in 90/10 DMSO-D_6/methanol-D_4, 2 min. after mixing with sodium methoxide-D_3 (2.5×10^{-1} mol.dm.$^{-3}$).

C Spectrum 6 min. after mixing.

D Spectrum 30 min. after mixing.

similar size shift occurred with the methylene group of HNBB on formation of the 3- σ -adduct, then its signal was part of the broad peak around δ 3.4 ppm.

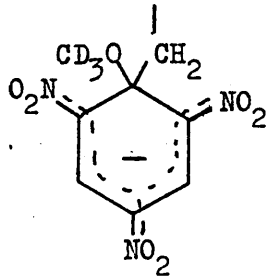
Since there were discrete resonances for HNBB and the 3- σ -adduct in the same solution, the complex must have a reasonably long lifetime compared to the ^{1}HNMR timescale. The results can be represented by an equilibrium (eqn 3), where the rate of the reverse reaction is slow.



(eqn 3)

If such an equilibrium was relatively rapid one would expect signals which were a weighted average of the frequencies of the complexed and uncomplexed protons.

Six minutes after mixing the reactants, Fig. 2.6.C., the spectrum of the 3- σ -adduct had decayed and been replaced by other signals. The signal at δ 8.6 ppm was at the position expected for the aromatic protons of a σ-complex formed by base attack at the 1-position on the trinitroaromatic ring (16).

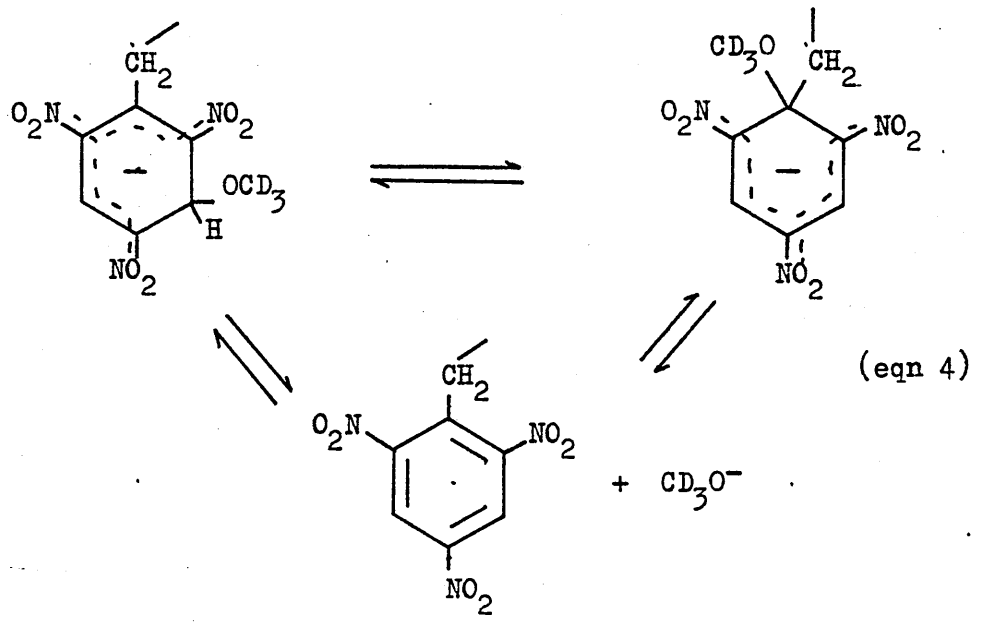


(16)

The signal at δ 2.7 ppm was assigned to the methylene group of such a 1- σ -adduct for the following reasons. A shift to higher field from δ 3.4 ppm in HNBB, would be expected because of the change

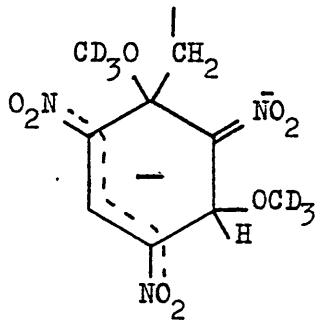
in hybridisation at the 1-position. Such a shift was observed in the signal of the methylene group of TNBCl on formation of a 1- σ -complex[37]. No 1- σ -adduct has been observed with TNT but the 3- σ -adduct formed from TNT and amide ion in liquid ammonia reacts with a second amide ion at the 1-position to yield a 1,3- σ -adduct[36]. The methyl signal in this complex shifted from δ 2.23 ppm in TNT to δ 1.62 ppm.

The ^{1}HNMR results thus confirmed the visible spectroscopic identification of a σ-complex from HNBB and base in polar aprotic solvents. The ^{1}HNMR spectra were, however, much more specific. They showed that initially the 3- σ -adduct (15) was formed, then this transformed into the 1- σ -adduct (16), an example of the kinetically favoured product changing to the more thermodynamically stable product. Whether the transformation involved both complexes in equilibrium with HNBB and methoxide-D_3 or whether the 3- σ -complex was a precursor to the 1- σ -adduct was not clear (eqn 4).



(eqn 4)

Direct conversion might involve an intermediate such as (17). A similar diadduct has been reported from the reaction of TNT with amide ion in liquid ammonia[36]. Such an intermediate might be the source of the signal at δ 8.1 ppm in Fig. 2.6.C.

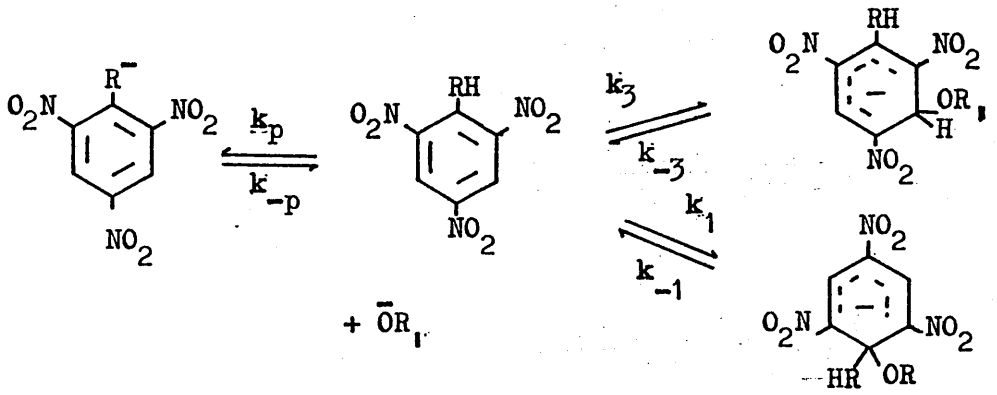


(17)

The reason for the greater stability of the 1- σ -adduct of HNBB lay in the relief of strain when the bulky trinitrobenzyl groups were moved more out of the way of each other, on the change of hybridisation at the 1-ring carbon. This fact, coupled with the greater inductive electron withdrawing effect of the trinitrobenzyl group, might be thought to make the 1-position more susceptible to nucleophilic attack than the 3-position. But attack at the 3-position occurred faster, probably because the transition state to the 3- σ -adduct was less strained and therefore of lower energy than that for the 1- σ -adduct.

As with HNBB, inductive and steric effects meant that the σ -adduct formed by alkoxide attack at the 1-position of TNBCl had greater thermodynamic stability than that formed by addition at the 3-position, Table 2.2[37]. This contrasted with the behaviour of TNT where σ -adducts were only observed from base attack at the 3-position. The rate of attack at the 3-position of TNBCl was faster than attack at the 1-position, but the main difference was in the rate of alkoxide departure, expulsion from the 1-position being considerably slower than from the 3-position.

The spectrum of the HNBB 1- σ -complex, Fig. 2.6.c., was similar to that seen in the later stages of the reaction of TNT with base, Fig. 2.5.c. The slight differences between the two were due to the small differences in solvent, base and base concentration between the two systems.



TNBCl : R = -CHCl

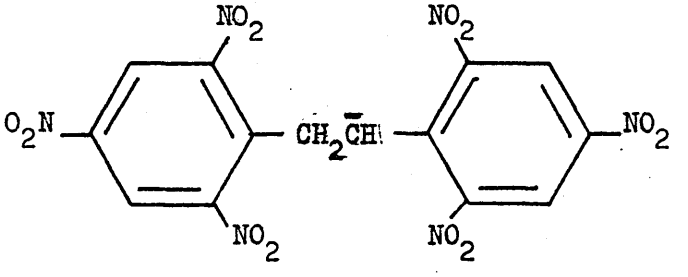
TNT : R = $-CH_2$

	k_3 $dm^3.mol.^{-1}S.^{-1}$	k_{-3} $S.^{-1}$	K_3 $dm^3.mol.^{-1}$	k_1 $dm^3.mol.^{-1}S.^{-1}$	k_{-1} $S.^{-1}$	K_1 $dm^3.mol.^{-1}$	k_p $dm^3.mol.^{-1}S.^{-1}$	k_{-p} $S.^{-1}$	K_p $dm^3.mol.^{-1}$
$TNBCl/\bar{O}CH_3$	-	-	< 20	770	2.2	350	16	0.065	250
$TNT/\bar{O}CH_3$	280	3000	0.07	-	-	-	13.3	1.1	12.4
$TNBCl/\bar{O}CH_2CH_3$	10,000	14	700	7000	<1	>10,000	-	-	-
$TNT/\bar{O}CH_2CH_3$	-	-	-	-	-	-	82	0.045	1800

Table 2.2 Comparison of the reactions of TNT and TNBCl with sodium methoxide in methanol and sodium ethoxide in ethanol at 25°C.[37]

Further changes occurred in the ^{1}HNMR spectrum of the basic HNBB solution. Over the next 20 mins. the signals assigned to σ-complexes gradually decayed and two new signals became established, Fig. 2.6.D. A sharp signal at δ 9.0 ppm and a broad one around δ 4.4 ppm. The solution was dark blue.

Now, in the reactions of base with polynitroaromatic compounds an alternative to σ-complex formation is proton abstraction to yield a carbanion. Does HNBB ionise in basic aprotic media and is Fig. 2.6.D consistent with an HNBB carbanion (13)?



(13)

In the reaction of TNT with methoxide ion the 3- σ -adduct was initially formed but decayed away to give the thermodynamically stable product of the reaction, TNT^-. The reaction of TNBCl with methoxide ion resulted in the formation at equilibrium, of both the 1- σ -adduct and the conjugate base of TNBCl. ^{1}HNMR evidence has been reported[69] on carbanions generated by addition of a solution of sodium methoxide in methanol to DMSO solutions of polynitrodiphenylmethanes (eqn 5), Table 2.1.

$$PiCH_2Ar + CH_3O^- \rightleftharpoons PiC\bar{H}Ar + CH_3OH$$

(eqn 5)

HNBB can be regarded as a substituted trinitrobenzyl derivative like TNBCl and its anion might be expected to have a similar spectrum to that of $TNBCl^-$, with additional resonances due to the extra trinitrobenzyl group. In other words, a quite complicated spectrum might be expected, not at all like the spectrum in Fig. 2.6.D.

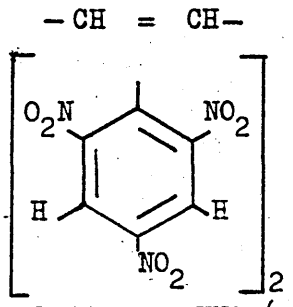
By the time the spectrum in Fig. 2.6.D had become established the solution was dark blue and HNS had begun to be precipitated. Is the spectrum due to some product from the interaction of HNS and base?

HNS

The ^{1}HNMR spectrum of HNS in DMSO-D_6 showed two singlets:

δ 7.2 ppm 2H

δ 9.2 ppm 4H



(Fig. 2.7.A.)

The spectrum of a saturated solution of HNS ($\sim 1 \times 10^{-1}$ mol.dm.$^{-3}$) in the presence of sodium methoxide-D_3 (2×10^{-1} mol.dm.$^{-3}$) in 90/10 DMSO-D_6/methanol-D_4, is shown in Fig. 2.7.B. The spectrum had signals around δ 9.1 and 7.2 ppm from unreacted HNS and weak signals at δ 9.0 and 6.2 ppm and a doublet around δ 8.5 ppm. These weak signals quickly disappeared and over the next 15 mins. the stronger signal at δ 9.1 ppm broadened until it too could not be seen, Fig. 2.7.C. The colour of the solution was red-brown from start to finish.

Thus, a result similar to Fig. 2.6.D, from the later stages of the reaction of HNBB with base, was not seen during the reaction of HNS with methoxide ion. This suggested that the species responsible for spectrum Fig. 2.6.D was formed during the dehydrogenation of HNBB to HNS and not from subsequent reactions of HNS.

As for the identify of the species responsible for the ^{1}HNMR spectra

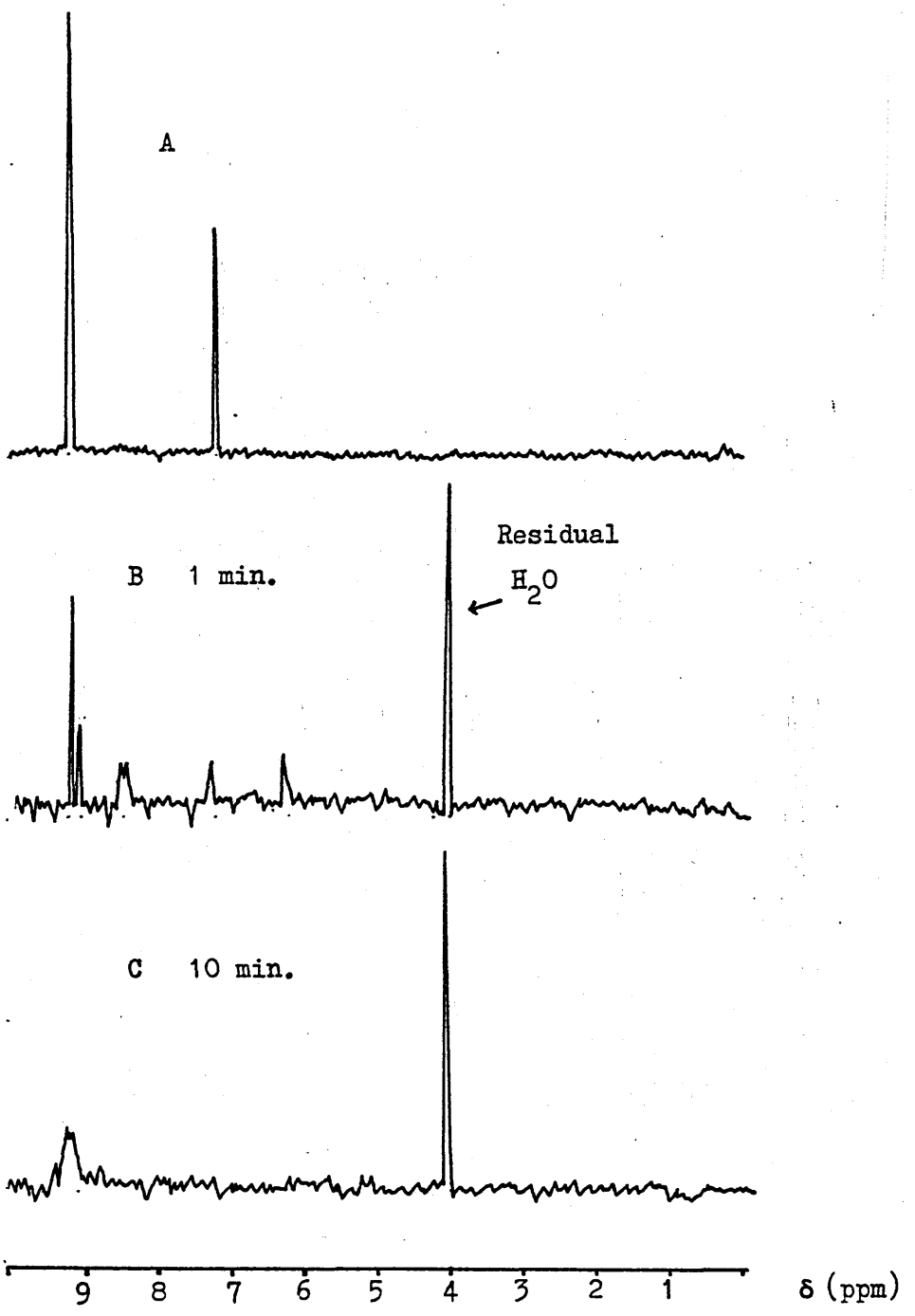
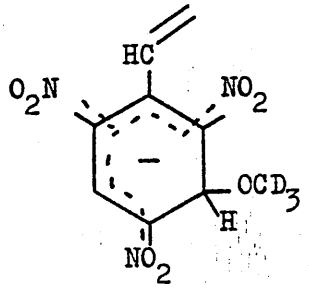


Fig. 2.7 A ^{1}HNMR spectrum of HNS in DMSO-D_6

B Spectrum of HNS (saturated solution) in 90/10 DMSO-D_6/ methanol-D_4, 1 min. after mixing with sodium methoxide-D_3 (2×10^{-1} mol.dm.$^{-3}$)

C Spectrum 10 min. after mixing.

from HNS in basic solution, Weak, transient signals made it difficult to give accurate assignments. Perhaps the most characteristic resonance absorption was that at δ 6.2 ppm, Fig. 2.7.B. From inspection of Table 2.1 and comparison with the behaviour of HNBB in similar conditions, this signal was assigned to the ring proton at the site of base attack in a 3- σ -complex (18).



(18)

This was consistent with the evidence from visible spectroscopy, which implied that HNS reacted with base to form a σ -complex.

To summarise, ^{1}HNMR confirmed the results from visible spectroscopy but much more information was gained on the nature of the products from the interaction of HNBB with base. ^{1}HNMR spectra showed that the initially formed 3- σ -complex transformed into a 1- σ -adduct with time. The broadening of signals in the spectra of basic solutions of TNT, HNBB and HNS suggested that radicals were present in the systems.

NMR did not resolve the question of the identity of the blue species. TNT, TNBCl and polynitrodiphenylmethanes all ionise in basic aprotic media, thus the HNBB carbanion (13) might be the source of the blue colour, although the evidence from visible and ^{1}HNMR spectroscopy suggest that this is unlikely. However, this possibility was tested further by hydrogen-deuterium exchange experiments.

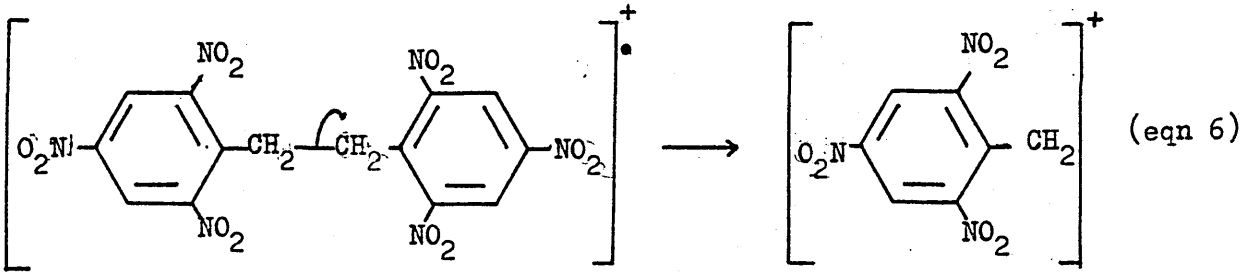
2.4.3 Hydrogen-Deuterium Exchange

TNT readily underwent hydrogen-deuterium exchange in basic 90/10 DMF-deuterium oxide[24]. If ionisation of a methylene proton of HNBB was an important pathway in its reaction with base and dehydrogenation to HNS, it too might be expected to undergo exchange, under conditions similar to those used to observe exchange with TNT.

A reaction mixture containing HNBB (2.4×10^{-1} mol.dm.$^{-3}$) and sodium methoxide-D_3 (2.4×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol-D_4 at 55°C, was quenched in deuterated acid, 1 min. after mixing the reactants. HNBB was recovered from the resulting precipitate by recrystallisation. The deuterium content of this recovered HNBB was deduced by mass spectrometry, infra-red and ^{1}HNMR spectroscopy.

Mass Spectrometry

No molecular ion was seen in the 70 eV mass spectrum of HNBB. Instead, the molecule underwent a simple fission process to produce an abundant ion at ^{m}/e 226 (eqn 6).



(eqn 6)

The carbon-13 isotope peak associated with this ion, at ^{m}/e 227, had an abundance of about 10% of that of the ion at ^{m}/e 226. The HNBB recovered from the exchange experiments had a much higher value, around 60%, for the ratio of the abundance of the ion at ^{m}/e 227 to the ion at ^{m}/e 226, showing that deuterium had been incorporated into the recovered HNBB, Fig. 2.8.

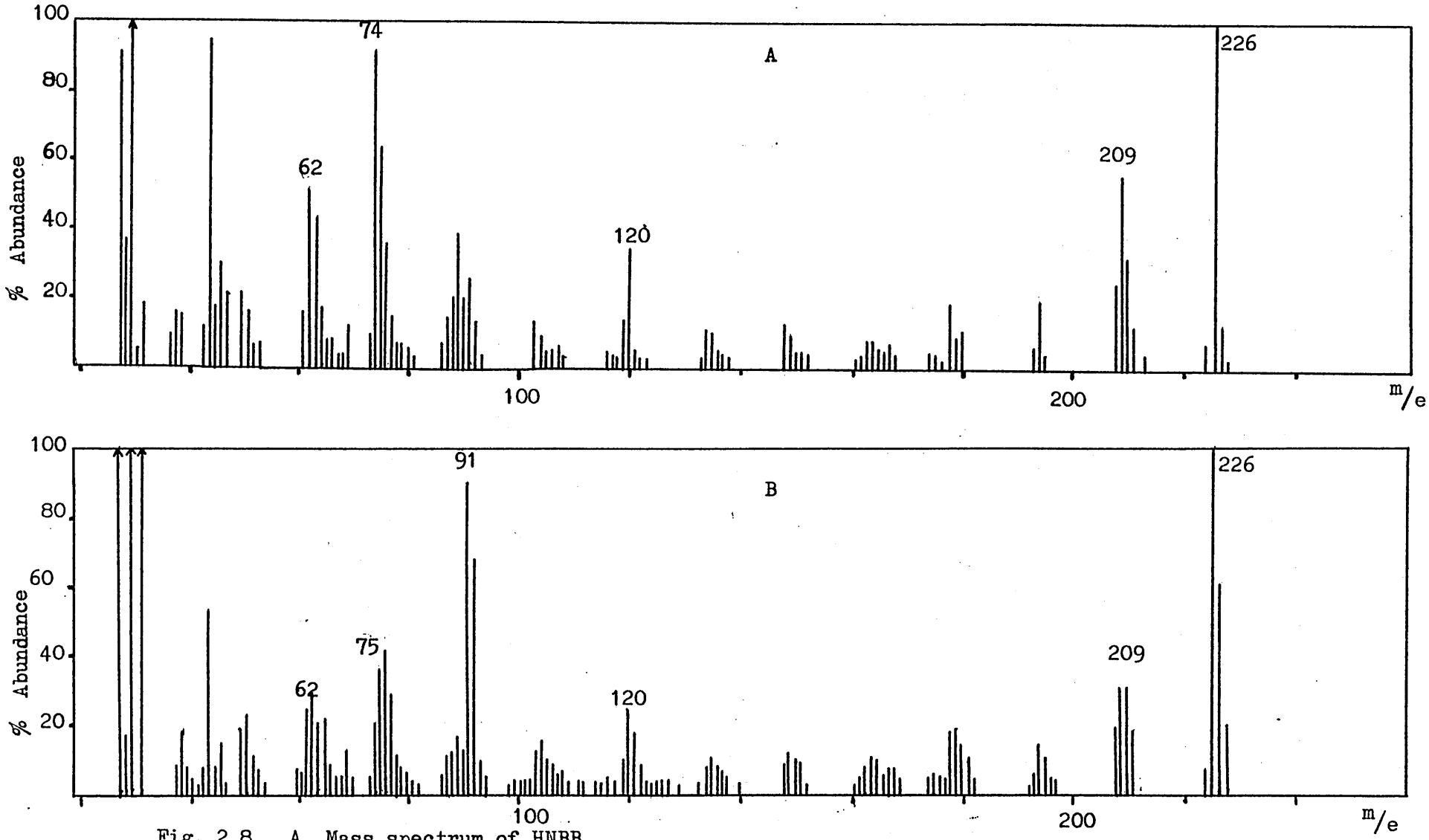


Fig. 2.8. A. Mass spectrum of HNBB

B. Mass spectrum of HNBB recovered from H/D exchange experiment

Infra-Red

Fig. 2.9 shows infra-red spectra of HNBB and HNBB recovered from an exchange experiment. Since the stretching frequency of a bond depends on the mass of the atoms undergoing oscillation, exchanging a proton for a deuteron will give rise to a C-D stretching band at a lower frequency than the original C-H stretching band. In fact, C-D bands appear at $^1/1.37$ times the corresponding C-H frequency.

Thus, if HNBB exchanged methylene protons for deuterons a new band would appear in the infra-red spectrum of the product at $^1/1.37$ times 2900 cm^{-1} (the C-H stretching frequency of the methylene protons), that is, round 2120 cm^{-1}. The new absorption band in the spectrum of the recovered HNBB actually occurred around 2300 cm^{-1}, which was close to the value expected for the C-D stretching frequency if an aromatic proton of HNBB, stretching frequency 3100 cm^{-1}, had been replaced by deuterium.

^{1}HNMR

Mass spectrometry had shown that deuterium had been incorporated into HNBB recovered from an exchange experiment and the infra-red spectrum of the product supported the proposition that the deuterium had gone, not into the methylene group of HNBB, but into the aromatic rings of the molecule. ^{1}HNMR was used to confirm this result and to estimate how much exchange had occurred.

An accurate weight of HNBB was dissolved in a known volume of deuterated acetone spiked with methylene chloride as an internal standard and the ^{1}HNMR spectrum of the solution recorded with integration. The ratios of the areas of the aromatic and methylene signals to the methylene chloride signal were calculated.

The same weight of recovered HNBB was then dissolved in the same volume of solvent and the ^{1}HNMR spectrum of this solution was recorded

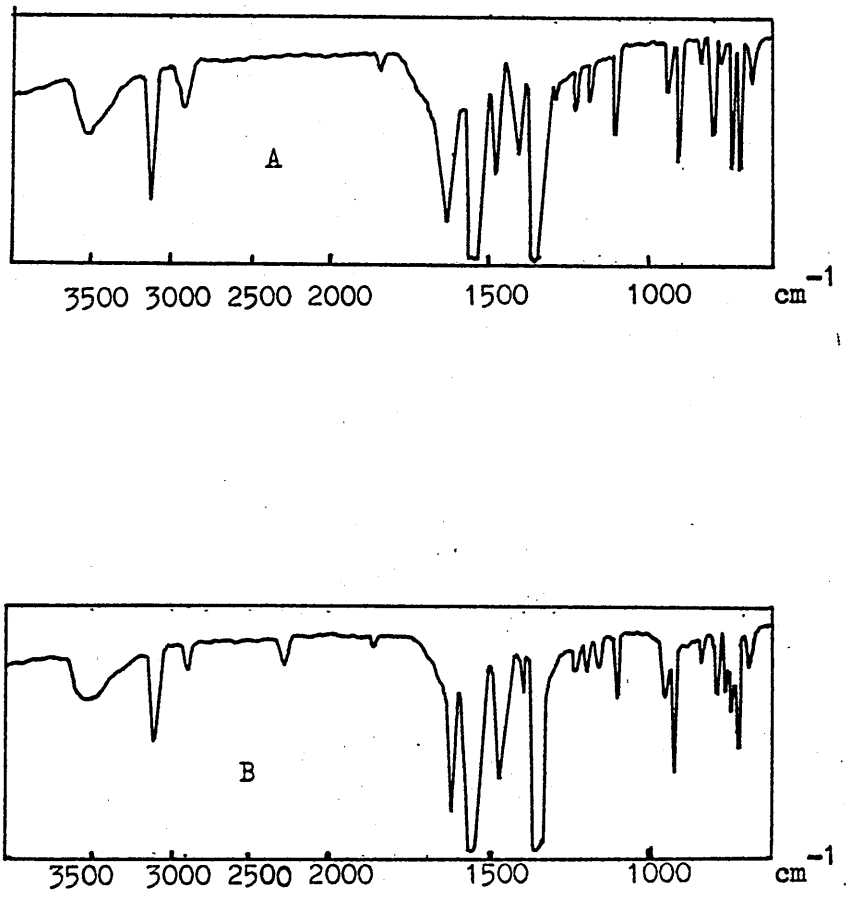


Fig. 2.9 A. Infra-red spectrum of HNBB

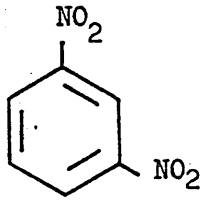
B. Infra-red spectrum of HNBB recovered from H/D exchange experiment.

with integration using the same conditions as for HNBB. Again, the ratios of the areas of the aromatic and methylene signals to the internal standard signal were calculated.

	HNBB	Recovered HNBB
Ar-H/CH_2Cl_2	1.10	0.76
$-CH_2-CH_2-/CH_2Cl_2$	1.10	1.00

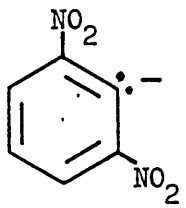
The results showed the aromatic signal of the recovered HNBB to be about 24% less intense than that of HNBB, the methylene signal was virtually unaffected. So, there was no evidence that any of the methylene protons of the recovered HNBB had been involved in exchange, but around 1 in 4 of the aromatic protons of the recovered HNBB had been replaced by deuterium. This is equivalent to a quantitative conversion of HNBB to a monodeuterated HNBB, although this need not necessary be the case, some molecules may contain more than one deuterium atom.

Hydrogen exchange involving the aromatic protons of nitroaromatic-compounds is not unknown. Hydrogen exchange in 1,3 - dinitrobenzene (DNB, 19) has been well established.



(19)

The solvent systems studied in this case have included, NaOD-D_2O-DMF[43], methanol-D_2O[44], DMSO-D_2O[45] and 1,2-dimethoxyethane-D_2O[45]. The anion (20) resulting from proton loss from the aromatic ring of DNB, was thought to be responsible for the colour of alkaline solutions of the compound[43].

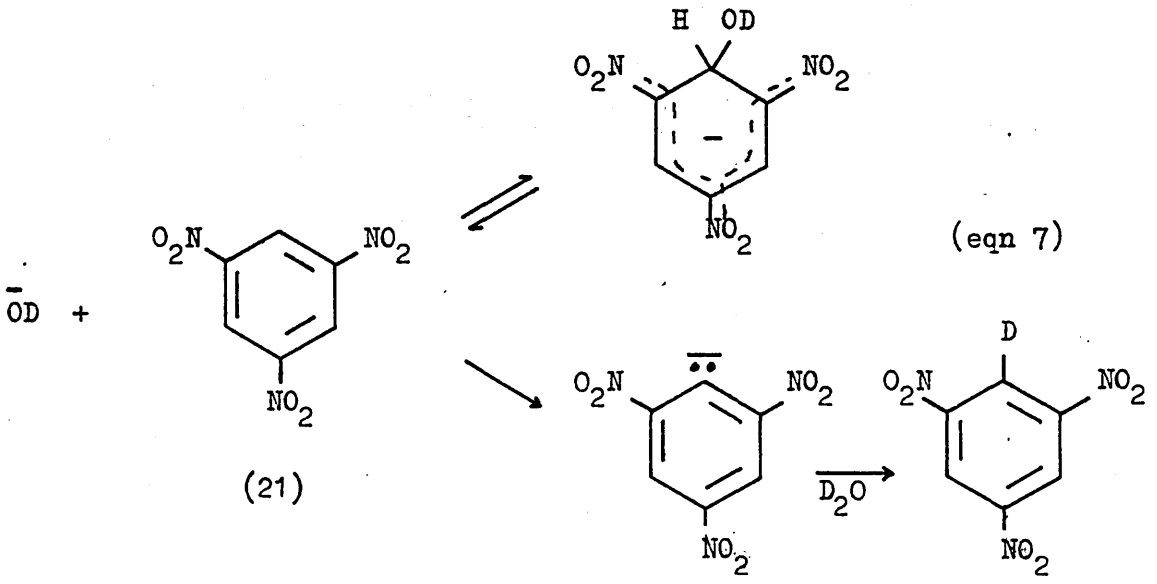


(20)

A later study of the relationship between hydrogen exchange and colour formation in DNB, showed that ions such as (20) were not responsible for the colour formation[46].

In all these studies it was shown or assumed that exchange occurred only at the 2-position of DNB. Recent tritium exchange and NMR studies on DNB[47] have shown that, in a dioxan-methanol-water system, tritium was indeed specifically incorporated at C-2. But in the more basic hexamethylphosphoramide-methanol-water system, tritium was incorporated at C-4 (6) as well as C-2, the relative amounts were 7% and 93% respectively.

Hydrogen exchange has been observed with 1,3,5-trinitrobenzene (TNB, 21) in DMF-D_2O in the presence of sodium deuterioxide[48] and in tritiated methanol using sodium methoxide[46]. The rate of exchange between TNB and sodium deuterioxide in mixtures of DMF-D_2O was shown to decrease with increasing DMF content. At constant medium composition and base concentration the rate was halved on doubling the TNB concentration. This unusual behaviour arose from competition between proton exchange and σ-complex formation (eqn 7).



(21) (eqn 7)

Hydrogen-deuterium exchange experiments have shown that HNBB ionises in basic DMF solution but that an aromatic proton is removed, not a proton from the methylene groups. There is evidence that aromatic anions of polynitroaromatic compounds are not responsible for the colour formation in basic solutions of polynitroaromatic compounds. Thus, the question still remains, what is responsible for the blue colour?

The broadening of signals in the ^{1}HNMR spectra of basic solutions of TNT, HNBB and HNS suggested radicals were present. It is well established that nitroaromatic compounds can be converted into radical anions by accepting an electron from a strong base. Transitions by an unpaired electron between energy levels of a radical requires less energy than transitions of paired electrons of the parent molecule. Radicals therefore absorb light of longer wavelength than the parent molecule with the result that many of them are coloured. The source of the blue colour might be due to radicals produced from the nitro compounds. Electrochemical methods were used to test this, and to investigate the properties of the radicals from these polynitroaromatic compounds.

2.4.4 Electrochemical Methods

The aim of the work which follows was to generate radical anions of TNT, HNBB and HNS in isolation, investigate their properties and then apply this information to the investigation of the oxidative coupling reaction of TNT to HNBB and HNS. The method used to prepare solutions of the radical anions was controlled potential electrolysis of solutions of the nitrocompounds in polar aprotic solvents (eqn 8).

$$\text{NITROAROMATIC} \xrightarrow{e^-} (\text{NITROAROMATIC})^{\pm} \qquad \text{(eqn 8)}$$

The technique of controlled potential electrolysis involves the measurement of the difference in potential between a working electrode and a reference electrode, and the adjustment of the voltage applied across the working and auxilliary electrodes in such a way as to keep this potential within certain limits. The apparatus used in this work is shown in Fig. 2.10.

It consisted of a pool of mercury as a relatively massive cathode, a platinum wire auxilliary electrode and a reference electrode constructed from a silver wire in a solution of tetraethylammonium perchlorate (0.1 mol.dm.$^{-3}$) in DMF. Contact was made between the reference electrode and the electrolysis solution by a liquid-liquid junction.

Because solutions of organic compounds are poor conductors the electrolysis solution contained a salt to carry most of the current, this electrolyte was tetraethylammonium perchlorate. A constant potential was achieved by connecting the electrodes to a potentiostat.

The limits within which the potential can vary are set by the need for a suitably high potential to ensure a satisfactory rate of electrolysis but not so high that alternative reactions occur. A suitable value for the potential can be deduced from polarography.

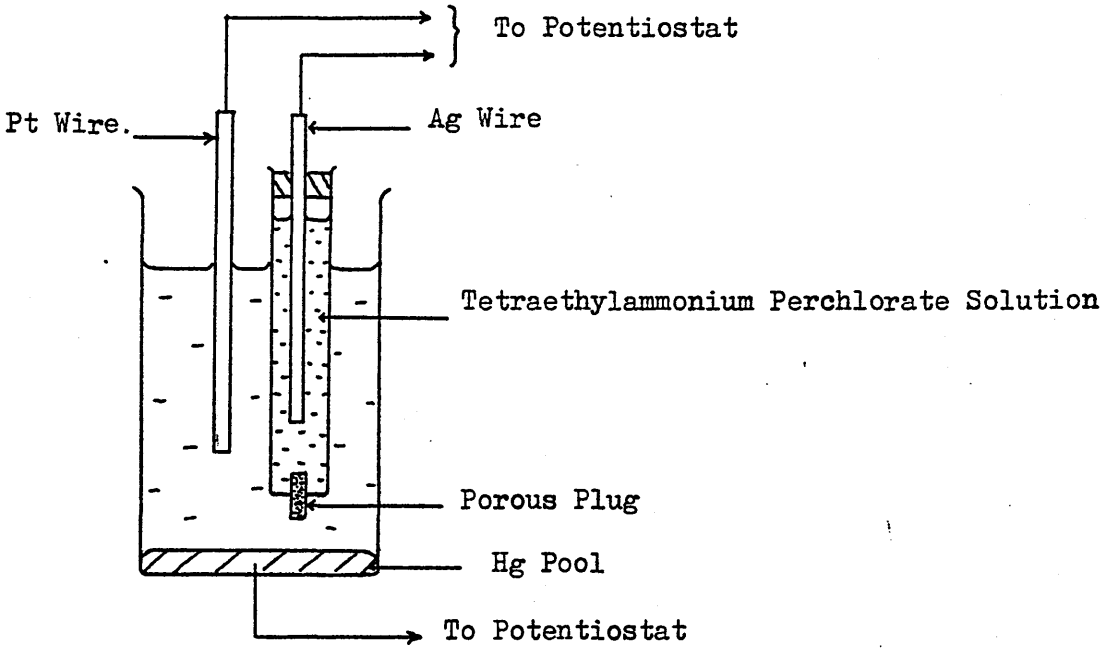


Fig. 2.10 Electrolysis Cell

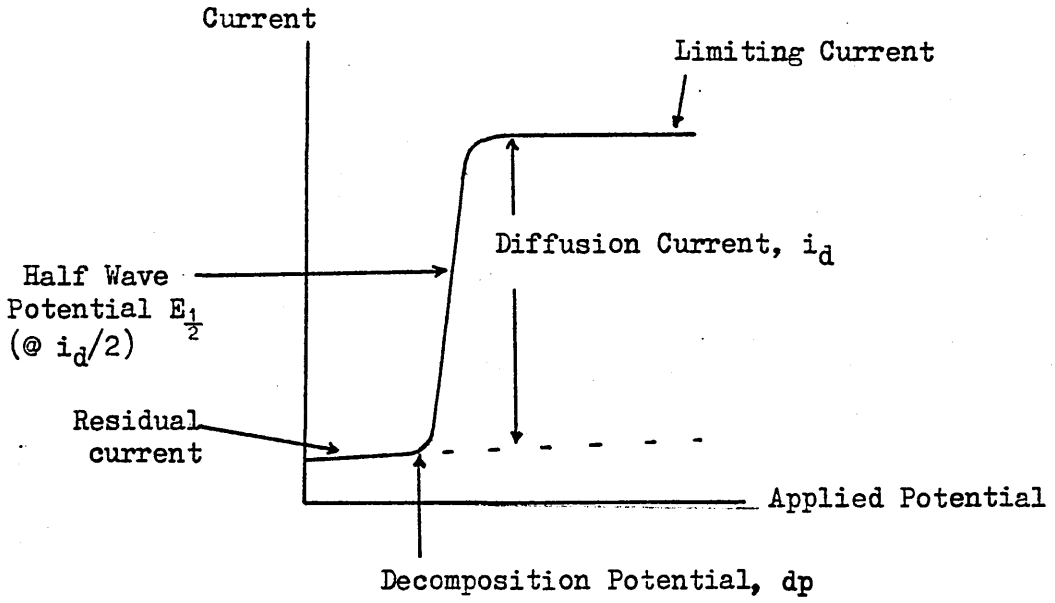


Fig. 2.11 A Polarogram

Polarographic data are obtained by measuring the current as a function of the potential applied to a special type of electrolytic cell containing a solution of the material of interest. A plot of the data gives current-voltage curves called polarograms, Fig. 2.11, which give qualitative and quantitative information about the composition of the solution in which the electrodes are immersed.

Only a residual current flows until the decomposition potential, dp, is reached. This is the potential at which reduction of the electroactive species in the film around the working electrode begins. Unreduced material diffuses from the bulk of the solution to replace the material that is reduced giving rise to a concentration gradient. As the applied potential is increased so the current increases and the rate of diffusion with it. Eventually a point is reached where there is no unreduced material in the film around the electrode and the diffusion rate becomes constant and is governed by the concentration of the solution, the current corresponding to this point is known as the constant diffusion current, id. The diffusion current is thus proportional to the concentration of reactant in solution. Of more interest for controlled potential electrolysis is the potential at which the electroactive species begins to be reduced. The half-wave potential, $E_{\frac{1}{2}}$, is the potential corresponding to a current that is equal to a half the diffusion current, id and is important for qualitative identification of the reactant. To obtain a reasonable rate of electrolysis the potential of the electrolysis cell must be greater than $E_{\frac{1}{2}}$ but not so great that other reactions start to occur. In the following experiments it was set at the potential at which the current became constant.

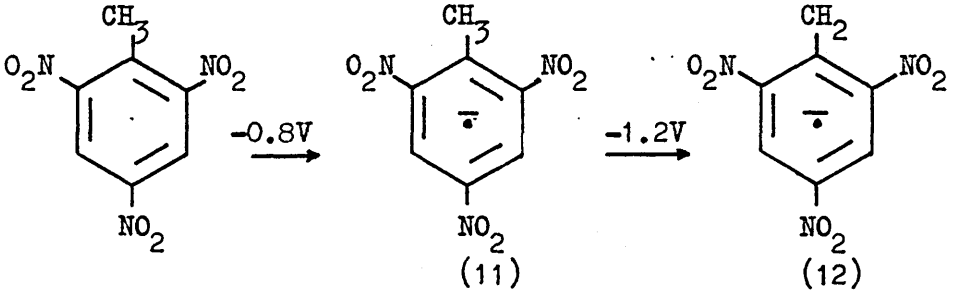
TNT

Polarography of TNT (1.5×10^{-4} mol.dm.$^{-3}$) in DMF containing

tetraethylammonium perchlorate (TEAP, 1 x 10^{-2} mol.dm.$^{-3}$) supporting electrolyte, produced three waves at half-wave potentials of -0.47V, -1.00V and -1.25V, Fig. 2.12.

Controlled potential electrolysis at -0.6V of TNT (4.3 x 10^{-2} mol.dm.$^{-3}$) in DMF containing TEAP (4.8 x 10^{-2} mol.dm.$^{-3}$) gave a purple solution with a visible spectrum, Fig. 2.13, similar to that of TNT^{-}. The spectrum had maxima at 520 nm and around 630 nm, the unreduced TNT absorbed strongly below 400 nm.

There have been few visible absorption studies of radical anions of nitroaromatic compounds. Most workers have used electrolysis as a method of generating radicals for further study by electron spin resonance spectroscopy (ESR). Thus, electrolytic reduction of TNT in DMF, DMSO and acetonitrile was reported to produce a radical species whose ESR spectrum was consistent with that of the TNT radical anion, $TNT^{\cdot -}$ (11)[40]. No information on the visible spectrum of this product was given. At more negative potentials a new spectrum appeared which was interpreted as the dinegative trinitrobenzyl radical (12) resulting from elimination of a methyl proton from $TNT^{\cdot -}$.



(11) (12)

In the present experiment either the visible spectrum of $TNT^{\cdot -}$ was similar to that of TNT^{-}, or the mechanism of the electrolytic reduction was more complex and produced TNT^{-} as the predominant product.

Instability of the initial reduction products of nitroaromatic compounds has been noted before. The first polarographic wave in the electrolytic reduction of nitromesitylenes (22) and nitrodurenes (23)

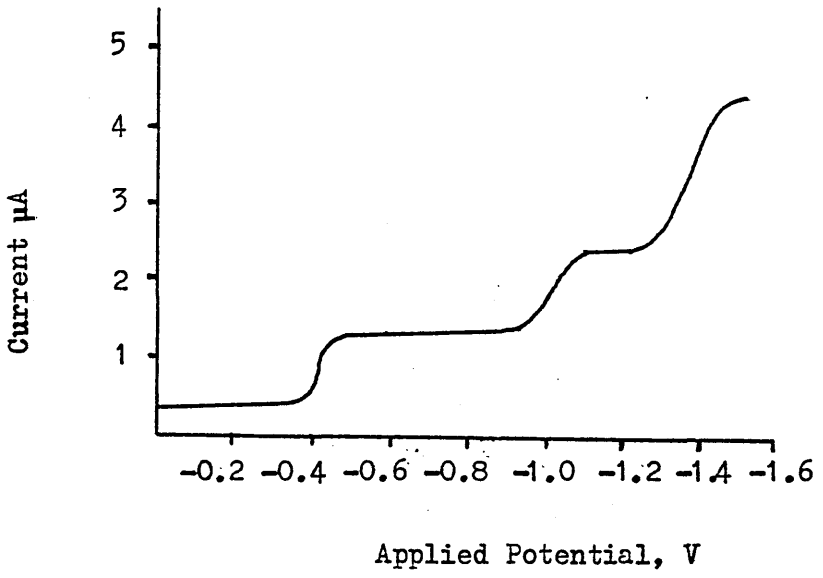


Fig. 2.12 Polarogram for TNT (1.5×10^{-4} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$).

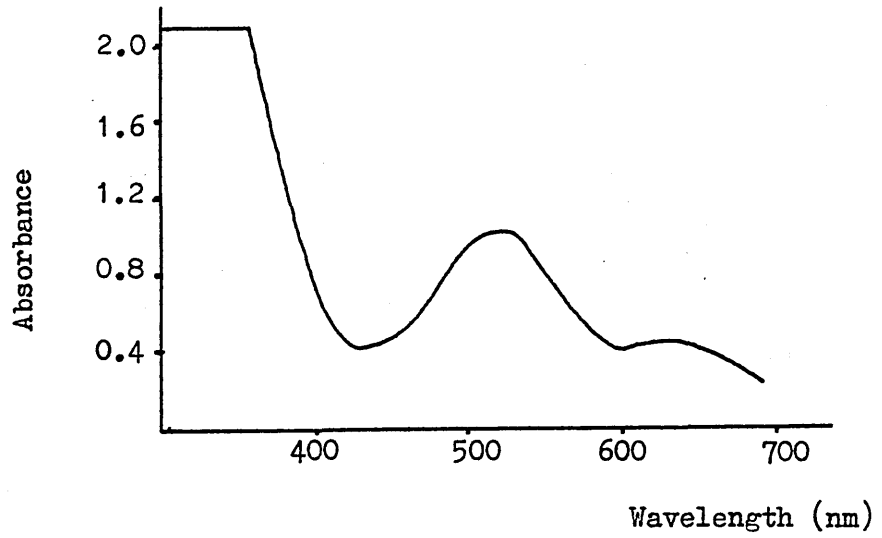
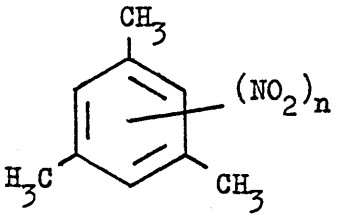
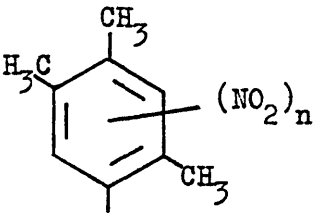


Fig. 2.13 Visible spectrum from electrolysis at -0.6V of TNT (4.3×10^{-2} mol.dm.$^{-3}$) in DMF containing TEAP (4.8×10^{-2} mol.dm.$^{-3}$).

in DMF corresponded to one electron reduction to form the radical anions of the compounds[49].



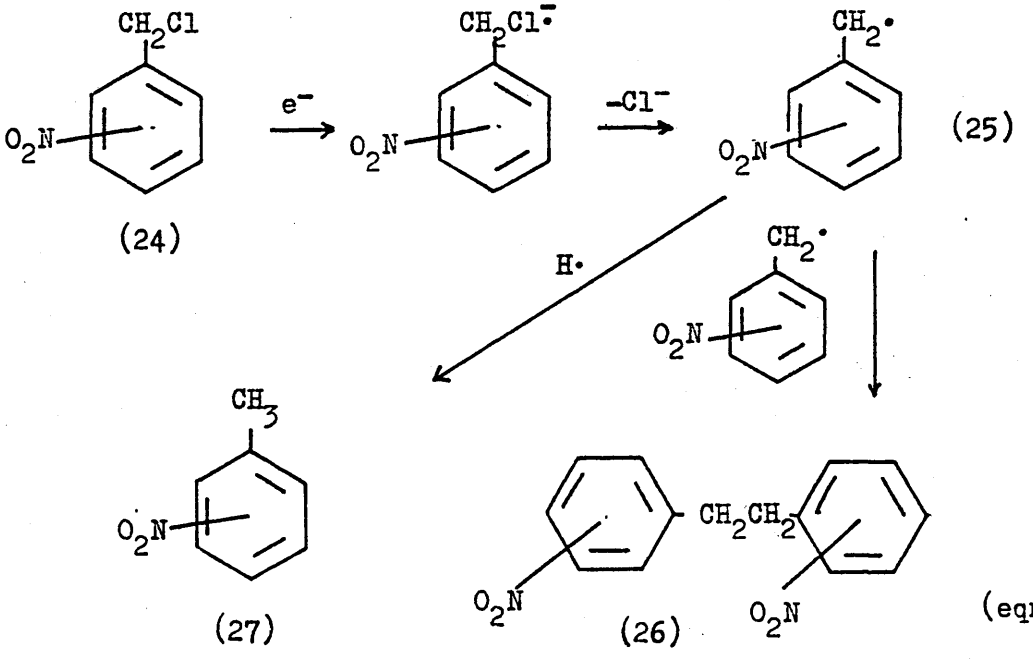
(22)



(23)

But at slightly more negative potentials reduction of nitro groups was observed to form nitroamine anions.

Nitrobenzyl chlorides (24) also formed radical anions on reduction in acetonitrile[50]. But the radical anions of 2- or 4-nitrobenzyl chlorides then lost chloride ion to yield nitrobenzyl radicals (25). These radicals then coupled to dinitrobibenzyls (26) or abstracted hydrogen from the solvent to form nitrotoluenes (27), (eqn 9).



(24) (25) (27) (26) (eqn 9)

The visible spectrum of the 4-nitrotoluene radical anion (28), produced by reduction or pulse radiolysis of 4-nitrotoluene in acetonitrile[51], had a broad maximum around 440 nm.

The visible spectrum of this radical was different from that of the 4-nitrobenzyl anion (29), which had an absorption maximum around 360 nm[52].

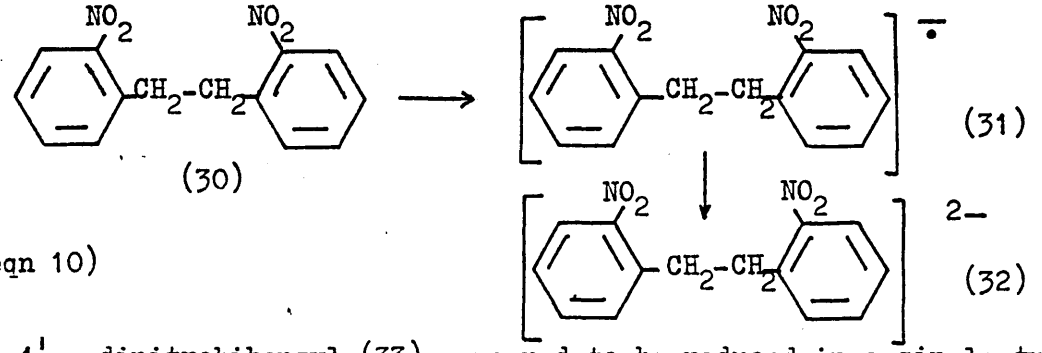
There is evidence, therefore, that radical anions can quickly undergo further reactions and that their visible spectra are different from those of the corresponding carbanions. The visible spectrum of the reduction product from TNT closely resembled that of TNT^-. It was concluded that the predominant reduction product from electrolysis of TNT under the conditions used, was TNT^- and that it was formed due to instability of the initially formed radical anion.

HNBB

Polarography of HNBB (2.4×10^{-4} mol.dm.$^{-3}$) in DMF in the presence of TEAP (1.0×10^{-2} mol.dm.$^{-3}$), gave three waves at half-wave potentials of -0.40V, -0.95V and -1.32V, Fig. 2.14.

Controlled potential electrolysis at -0.6V of HNBB (4.5×10^{-3} mol. dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$) gave a red-brown solution with a visible spectrum characteristic of a σ-complex, Fig. 2.15. The spectrum had maxima at 438 and 525 nm, with the extinction coefficient of the shorter wavelength band 1.8 times that of the other.

The reduction of dinitrobibenzyls has been studied[50]. Reduction of 2,2' - dinitrobibenzyl (30), in acetonitrile proceeded in two one-electron steps to yield a dianion (32) via a radical anion (31), (eqn 10).



(30) (31) (32)

(eqn 10)

4,4' - dinitrobibenzyl (33) appeared to be reduced in a single two electron transfer to give a dianion (34), (eqn 11).

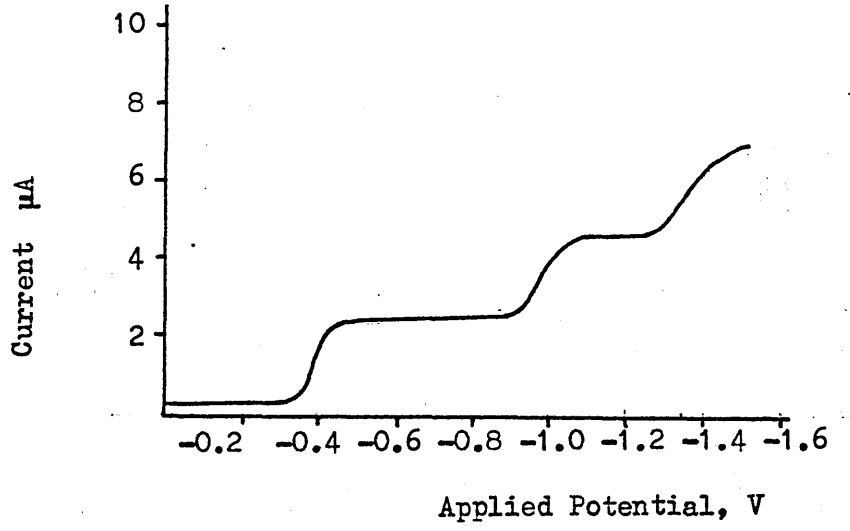


Fig. 2.14 Polarogram for HNBB (2.4×10^{-4} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$).

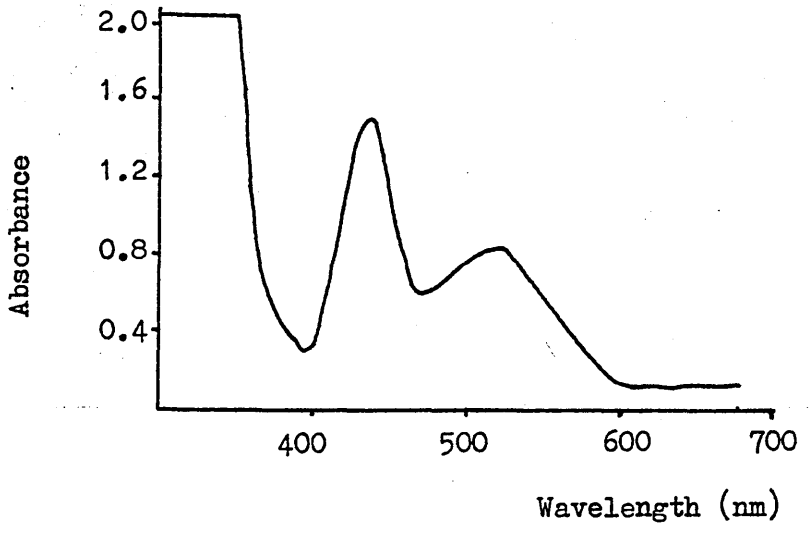
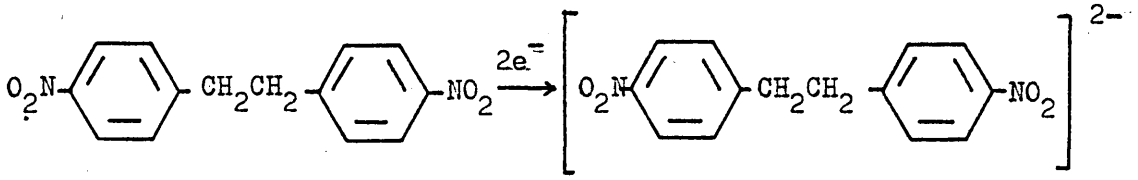


Fig. 2.15 Visible spectrum from electrolysis at -0.6V of HNBB (4.5×10^{-3} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$).



(33) (34) (eqn 11)

The visible spectrum of the reduction product of 4,4'-dinitrobibenzyl had a sharp maximum at 630 nm with a shoulder at 585 nm.

The reduction of HNBB did not proceed as straightforwardly as that of the dinitrobibenzyls. As with TNT, further reactions of the initially formed radical yielded what appeared to be a non-radical product. The evidence suggested that the predominant product from electrolytic reduction of HNBB was a σ-complex.

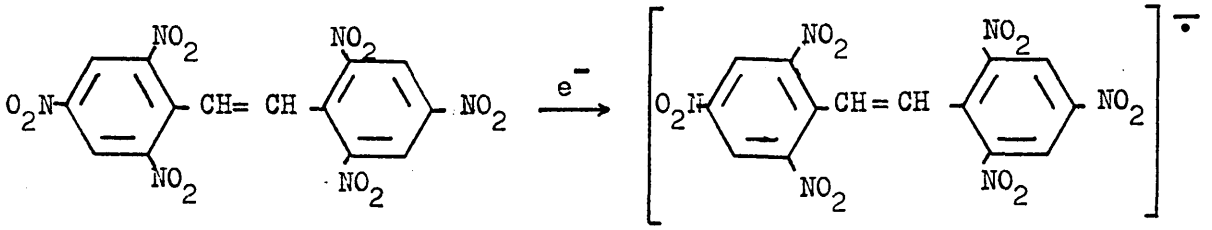
HNS

Polarography of HNS (2.4×10^{-4} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$) gave a well-defined wave at a half-wave potential of -0.6V and two ill-defined waves at around -1V and -1.2V, Fig. 2.16.

Controlled potential electrolysis at -0.7V of this solution gave a blue colour, the visible spectrum of which showed a broad maximum around 610 nm, Fig. 2.17.

This blue colour and visible spectrum were similar to those seen in the later stages of the reactions of TNT and HNBB with base, but which it had not been possible to generate from basic solutions of HNS.

The simplest mechanism for formation of the blue species was the one electron reduction of HNS to the HNS radical anion (35), (eqn 12).



(35) (eqn 12)

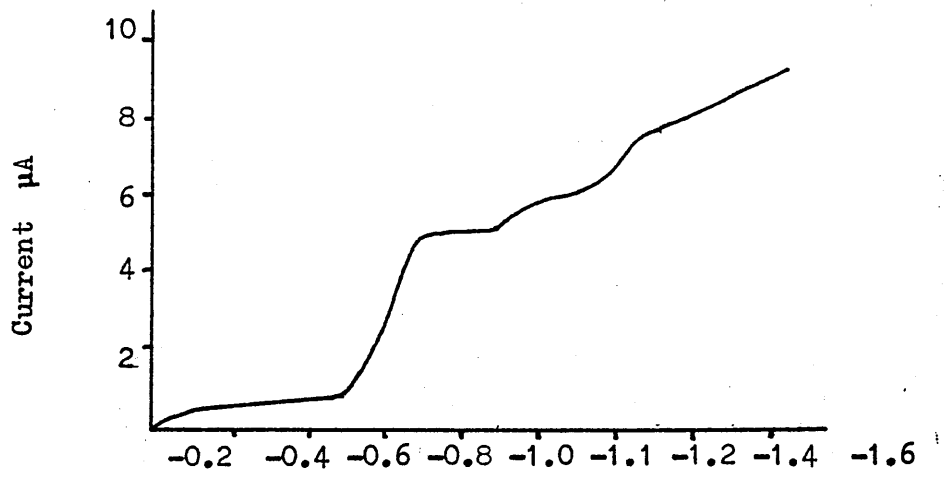


Fig. 2.16 Polarogram for HNS (2.4×10^{-4} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$)

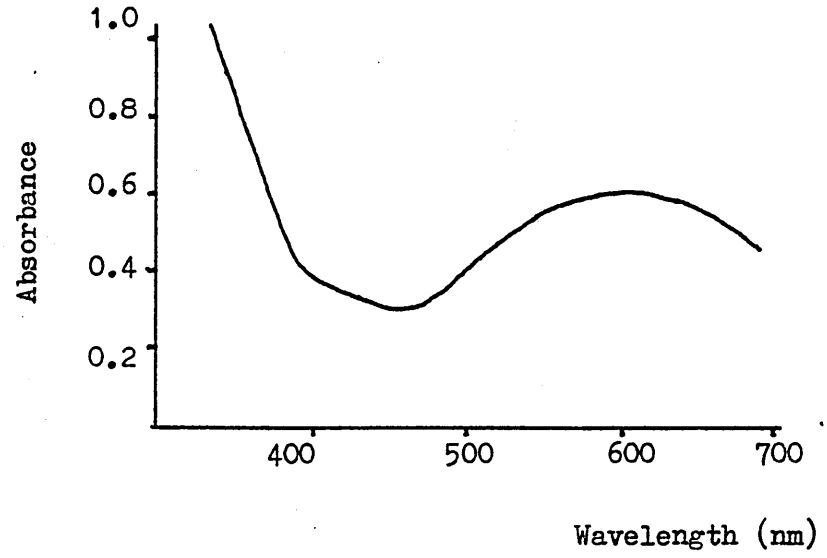


Fig. 2.17 Visible spectrum from electrolysis at -0.7V of HNS (2.4×10^{-4} mol.dm.$^{-3}$) in DMF containing TEAP (1×10^{-2} mol.dm.$^{-3}$)

The 4,4'-dinitrostilbene radical anion has been identified, by ESR, in the oxidation of 4-nitrotoluene to 4,4'-dinitrobibenzyl and 4,4'-dinitrostilbene[39]. There was no evidence of the 4,4'-dinitrobibenzyl radical anion which suggests that stilbene radical anions are more stable than radical anions of corresponding bibenzyls.

In summary, controlled potential electrolysis was used as a method of generating radical anions of TNT, HNBB and HNS. However, electrolysis of TNT gave a product whose visible spectrum matched that of TNT^- and electrolysis of HNBB produced a species with the visible spectrum of a σ-complex. These results suggested that the radical anions of TNT and HNBB once formed, underwent further reactions to yield other products which were responsible for the colour of the electrolysed solutions.

Electrolysis of HNS produced a blue solution with a visible spectrum which matched that from the latter stages of the Hungarian reaction and which it had been possible to produce from basic solutions of HNBB but not HNS. The blue colour was assigned to the HNS radical anion.

2.4.5 Concluding Remarks and Summary

Visible and ^{1}HNMR spectroscopy, hydrogen-deuterium exchange and electrochemical methods have identified some of the intermediates involved in the oxidation of TNT to HNBB and HNS by the Hungarian Patent method.

The transient brown colour seen at the start of the reaction was due to a 3- σ-complex of TNT which was quickly converted to the purple trinitrobenzyl anion. The purple colour was then itself replaced by the red-brown of a σ-complex of HNBB.

The interaction of HNBB with base initially formed a 3- σ-complex but with time this transformed into the thermodynamically preferred 1- σ-adduct. Although HNBB did ionise in basic DMF, hydrogen-deuterium exchange experiments showed that exchange occurred with aromatic but not with methylene protons.

HNS, like HNBB, yielded a 3- σ-complex on reaction with base but this species was not responsible for the blue colour which marked the final stages of the oxidation reaction. The visible spectrum of the reaction solution at this time matched that of a blue species produced by controlled potential electrolysis of HNS solution. This blue colour was assigned to the HNS radical anion.

In the reaction of TNT with potassium t-butoxide very little, if any σ-complex formation occurred, the predominant reaction being proton abstraction[28]. Although the preliminary interaction of HNBB with hydroxide and methoxide ions was σ-complex formation it might be expected that proton abstraction would be favoured with t-butoxide ions.

A reaction mixture containing HNBB (2×10^{-1} mol.dm.$^{-3}$) and potassium t-butoxide (2×10^{-1} mol.dm.$^{-3}$) in DMSO, went blue as soon as the reactants were mixed. The visible spectrum of a diluted sample from this mixture showed a broad maximum around 620 nm with a shoulder at 464 nm. The spectrum was similar to that assigned to the HNS radical anion, Fig. 2.17, which characterised the latter stages of the Hungarian reaction.

The ^{1}HNMR spectrum of HNBB (4.9×10^{-1} mol.dm.$^{-3}$) and potassium t-butoxide (6.7×10^{-1} mol.dm.$^{-3}$) in DMSO-D_6 showed a singlet at δ 8.6 ppm and a broad signal around δ 4.6 ppm. The signals of the protons of HNBB had disappeared. This spectrum was similar to that which finally became established in the HNBB-sodium methoxide-D_3 system, Fig. 2.6.D.

Thus it seems that the HNS radical anion was formed more readily from HNBB using potassium t-butoxide than from reaction with hydroxide or methoxide ions. This may point to the intermediacy of the HNBB carbanion (13) in the formation of HNS.

3. OXIDATION OF NITROAROMATIC COMPOUNDS

At its simplest the Hungarian method for the oxidation of TNT to HNBB and HNS involves ionisation of TNT to yield the trinitrobenzyl anion, which is consumed by a reaction with molecular oxygen, catalysed by copper ions. This chapter reviews the literature concerned with the reaction of organic compounds and molecular oxygen, with or without copper as a promoter and uses such information to discuss the results of a study of the oxidative coupling reaction of TNT.

3.1. The Reaction of Organic Compounds with Molecular Oxygen

3.1.1 Autoxidation[53]

Autoxidation is the reaction between molecular oxygen and organic compounds. It is a subject which has received considerable attention because of its importance in the drying of paints and oils and its relation to the undesirable processes of edible oils turning rancid and rubber perishing.

Autoxidation almost always results in the formation of hydroperoxides which may then decompose to yield alcohols, ketones and more complicated products (eqn 1).

$$RH + O_2 \longrightarrow ROOH \rightsquigarrow ROH,\ R_2C=O,\ \text{others} \qquad \text{(eqn 1)}$$

Most autoxidations involve a radical chain mechanism:

Initiation

$$\text{Initiator} \longrightarrow 2In^{\bullet}$$

$$In^{\bullet} + RH \longrightarrow R^{\bullet} + InH$$

Propagation

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \longrightarrow R^{\bullet} + ROOH$$

Termination

$$ROO\cdot + ROO\cdot \longrightarrow \text{non-radical products}$$

$$R\cdot + ROO\cdot \longrightarrow ROOR$$

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

3.1.2 The Reaction of Carbanions with Oxygen[54]

Studies of the reactions between oxygen and a variety of carbanions have led to the conclusion that in many cases oxidation involves a radical mechanism involving electron transfer from the carbanion ($R:^-$) to an electron acceptor (X), (eqn 2).

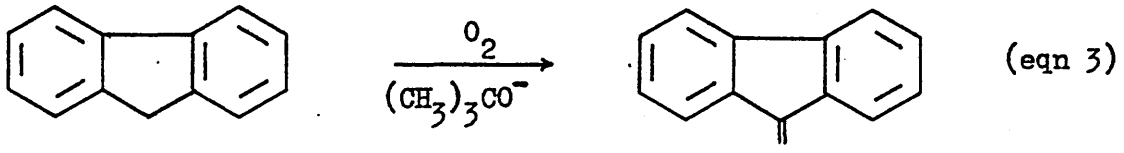
$$R:^- + X \longrightarrow R\cdot + X^- \qquad \text{(eqn 2)}$$

(where X may be: O_2; $ROO\cdot$; $RO\cdot$; $OH\cdot$)

Again, the products from such reactions are often alcohols and carbonyl compounds formed by decomposition of hydroperoxides. The oxidation of fluorene is typical.

Oxidation of Fluorene

Fluorene (1) is oxidised to fluorenone (2) by molecular oxygen in the presence of potassium t-butoxide in t-butanol solution (eqn 3).

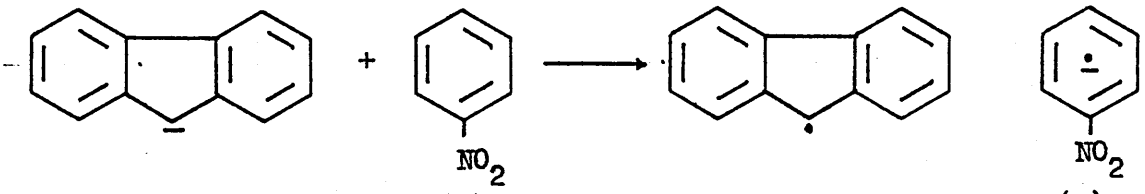


(eqn 3)

(1) (2)

The oxidation occurs more readily in mixtures of t-butanol with aprotic solvents such as dioxane, hexamethylphosphoramide (HMPA), DMF or DMSO. Such solvent effects are consistent with a process involving ionisation of fluorene to yield the fluorenide anion which then reacts with oxygen.

The rate of oxidation is greatly enhanced by the presence of small concentrations of nitroaromatic compounds. The reaction between the fluorenide anion (3) and nitrobenzene (4) was monitored by electron spin resonance spectroscopy (ESR). The spectrum observed was consistent with the formation of the nitrobenzene radical anion (5).



(3) (4) (5)

The following mechanism was proposed:

$$R_2CH_2 + B^- \rightleftharpoons R_2CH^- + HB$$

$$R_2CH^- + O_2 \longrightarrow R_2CH\cdot + O_2^-$$

(or nitroaromatic compound)

$$R_2CH\cdot + O_2 \longrightarrow R_2CHOO\cdot$$

$$2R_2CHOO\cdot \longrightarrow \text{products}$$

Oxidation of 4-Substituted Toluenes

A variety of substituted toluenes, $4\text{-}X\text{-}C_6H_4CH_3$, where X = C_6H_5CO-, NC-, $CH_3C_6H_5CO$-, $C_6H_5SO_2$-, $4\text{-}C_6H_4\text{-}N{=}N$-, or CH_3O_2C-, react with oxygen in basic solution to yield a mixture of the corresponding stilbene and carboxylic acid (eqn 4).

$$4 - X - C_6H_4CH_3 \xrightarrow[O_2]{\text{Base}} X - C_6H_4CH = CH - C_6H_4 - X + X - C_6H_4COOH$$

(eqn 4)

No saturated dimers, $X\text{-}C_6H_4CH_2\text{-}CH_2C_6H_4\text{-}X$ were found and the ratio of products was insensitive to the concentration of reactants used.

These results were thought to rule out a mechanism such as:

$$X - C_6H_4CH_3 \longrightarrow X - C_6H_4\bar{C}H_2 \longrightarrow X - C_6H_4CH_2^{\bullet} \longrightarrow$$

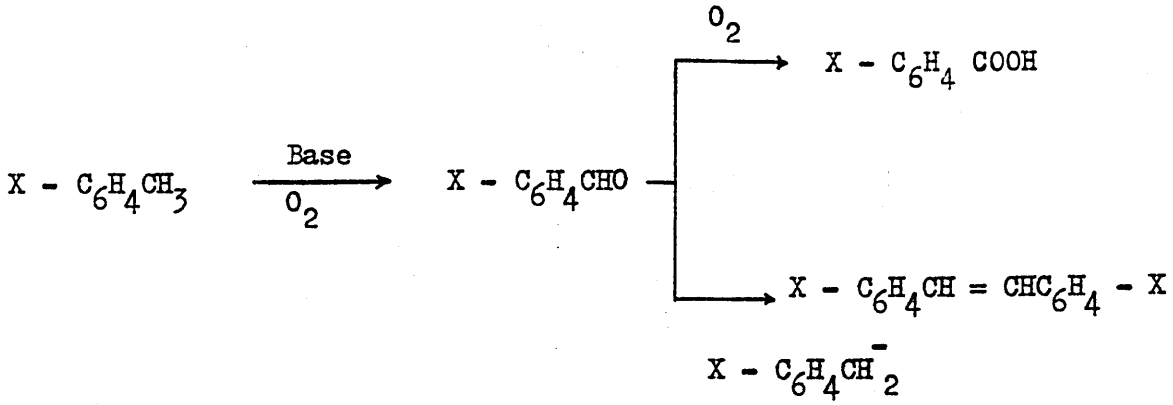
$$X - C_6H_4CH_2 - CH_2C_6H_4 - X \longrightarrow X - C_6H_4CH = CHC_6H_4 - X$$

It was well known that condensation of a toluene derivative with an aldehyde yielded a stilbene (eqn 5) and evidence for condensation between a toluene derivative and an intermediate aldehyde as the mechanism of oxidation of the toluene derivative came from reactions using labelled compounds.

$$X - C_6H_4CH_3 + X - C_6H_4CHO \xrightarrow{\text{Base}} X - C_6H_4CH = CHC_6H_4 - X$$

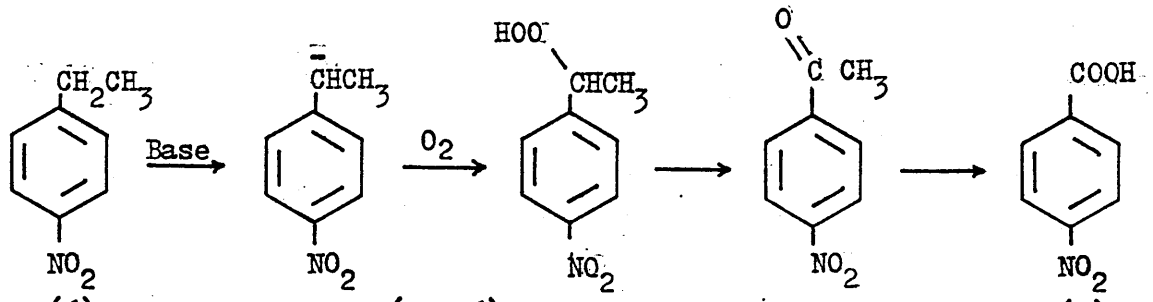
(eqn 5)

The addition of labelled 4-(phenylsulphonyl) benzaldehyde to an oxidation reaction of phenyl-4-tolylsulphone showed that the radioactive aldehyde was converted to 4-(phenylsulphonyl) benzoic acid and 4,4' - di(4-phenylsulphonyl) stilbene in the same ratio as phenyl-4-tolylsulphone was converted to the acid and the stilbene. Such results were consistent with the following mechanism for the oxidation of substituted toluenes:



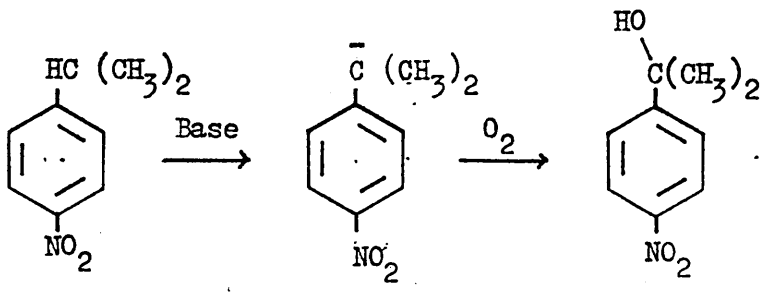
Oxidation of Nitrotoluenes[14,39]

Nitrotoluene derivatives which ionise to secondary or tertiary carbanions yield oxygenated products on reaction with oxygen. 4-Nitroethylbenzene (6) was oxidised less readily than 4-nitrotoluene in t-butanol containing potassium t-butoxide to give a high yield of 4-nitrobenzoic acid (7, eqn 6).



(6) (eqn 6) (7)

4-Nitrocumene (8) was oxidised to 4-nitro- α , α '-dimethylbenzyl alcohol (9) in 80/20 DMSO-t-butanol containing potassium t-butoxide (eqn 7),



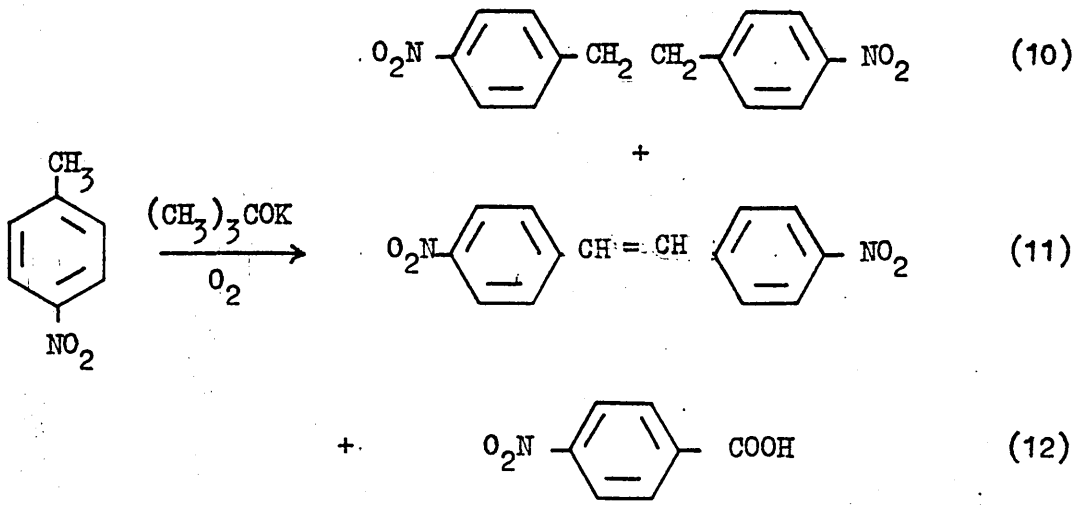
(8) (9) (eqn 7)

but was stable to oxygen in t-butanol containing potassium t-butoxide.

The oxidation of 4-nitrotoluene is atypical of that of other substituted toluenes in yielding saturated dimers.

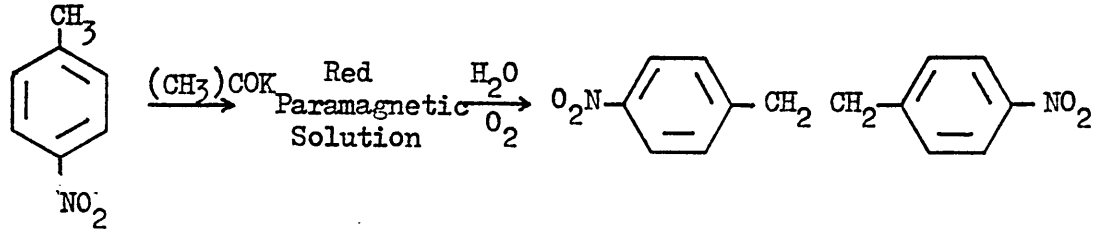
The Oxidation of 4-Nitrotoluene in Basic Solution

The reaction of 4-nitrotoluene in t-butanol and 80/20 dimethylsulphoxide-t-butanol has been studied in detail. In the presence of oxygen the reaction yields, 4,4' - dinitrobibenzyl (10, DNBB), 4,4' - dinitrostilbene (11, DNS) and 4-nitrobenzoic acid (12, eqn 8).



(eqn 8)

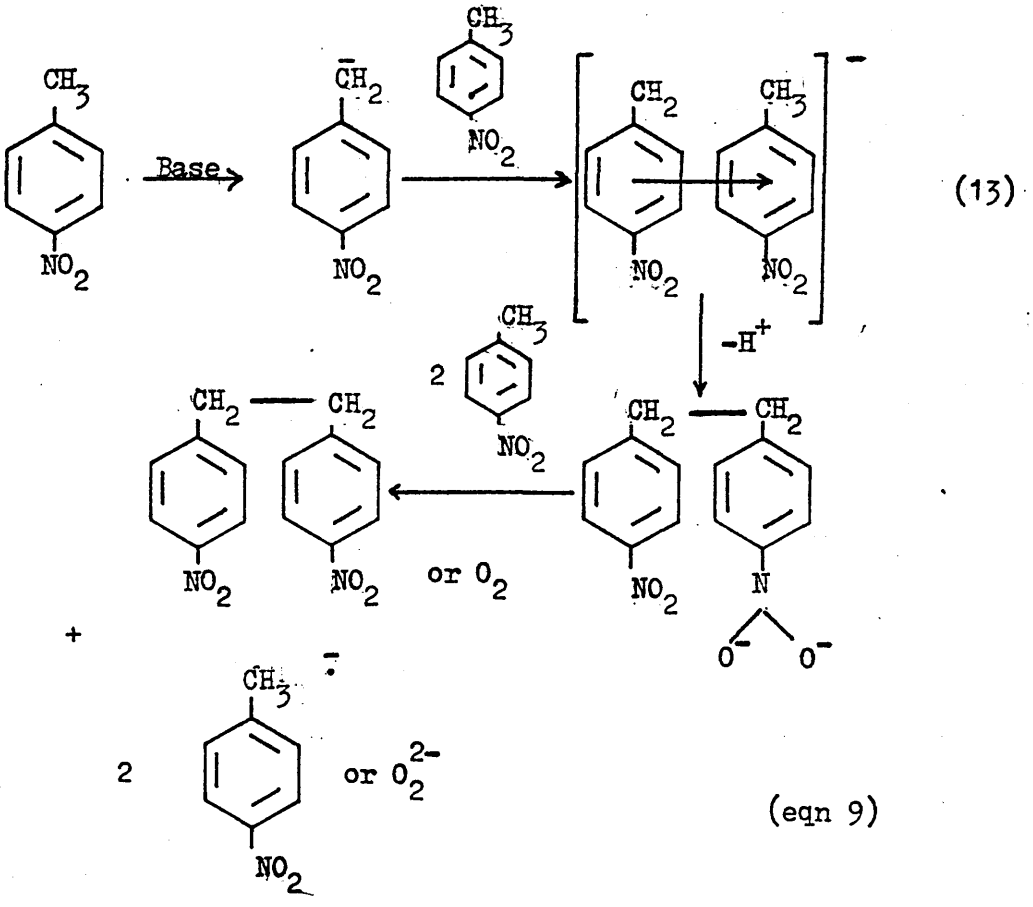
In the absence of oxygen a blood-red solution is produced which contains a large concentration of a paramagnetic substance. Treatment of this solution with water and oxygen yields DNBB :



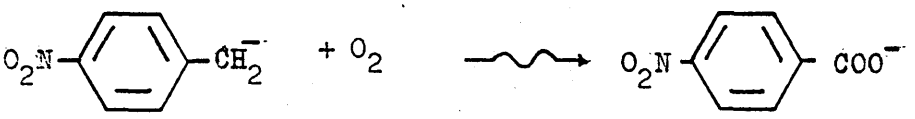
The kinetics of the reaction were followed by measuring the rate of oxygen absorption, the yield of products as a function of time and the increase in an ESR signal with time.

ESR also provided evidence for the presence of 4-nitrotoluene and DNS radical anions in solution. The initial yellow colour observed on mixing the reactants was assigned to the 4-nitrobenzyl anion. The red colour of the reaction mixture was thought to be due to the presence of the 4-nitrotoluene radical anion and a charge transfer complex derived from two 4-nitrotoluene molecules.

The experimental evidence was rationalised in a reaction mechanism which involved ionisation of 4-nitrotoluene and the formation of a charge-transfer complex (13) which decomposed to give DNBB and a 4-nitrotoluene radical anion (14, eqn 9).

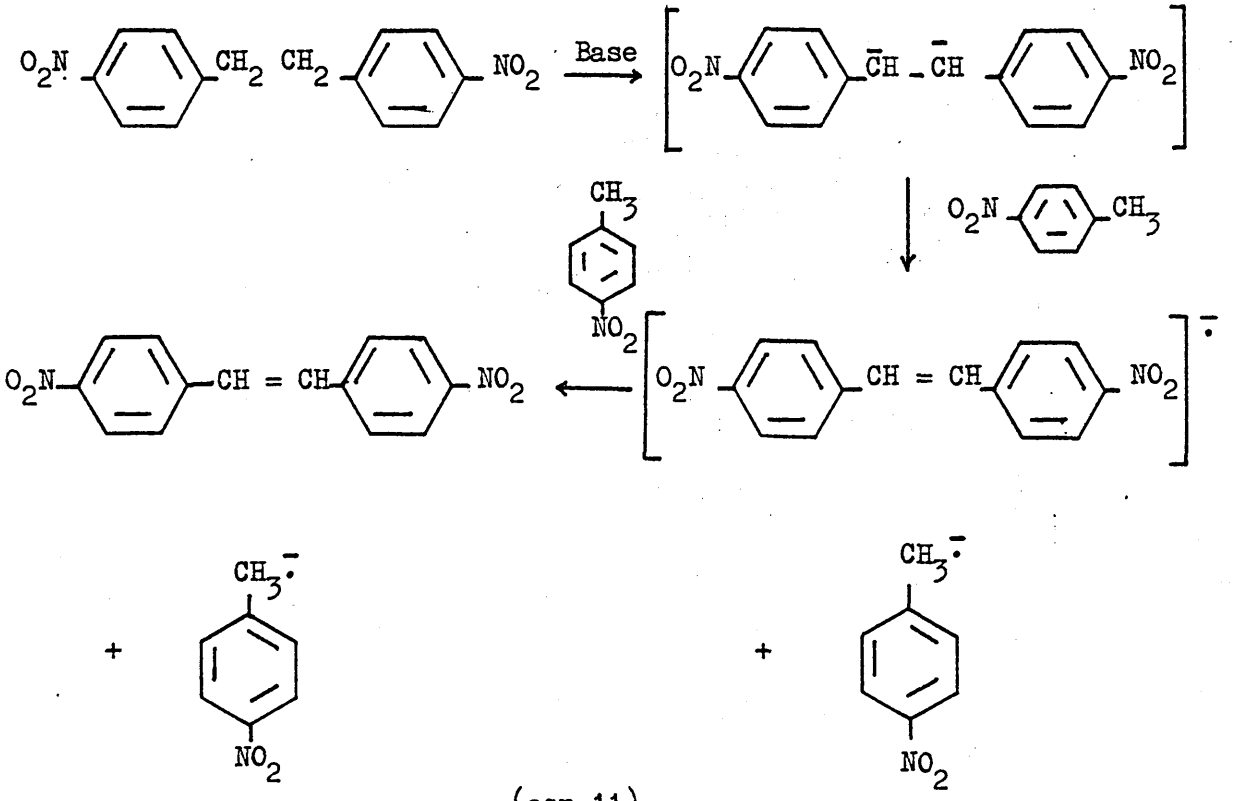


4-Nitrobenzoic acid was formed from a competing reaction in which oxygen combines with the 4-nitrobenzyl anion (eqn 10).



(eqn 10)

The mechanism proposed for DNS production involved ionisation of DNBB and then electron transfer reactions with 4-nitrotoluene (eqn 11).



(eqn 11)

Oxidation of Polynitrotoluenes[14,39]

TNT oxidised more slowly than 2,4-dinitrotoluene which in turn oxidised more slowly than 4-nitrotoluene in t-butanol containing potassium t-butoxide. Trace amounts of 2,4-dinitrophenol were formed from the oxidation of 2,4-dinitrotoluene but no coupling products were formed from either of the polynitrotoluenes.

The rate of oxidation was faster in 80/20 DMSO-t-butanol. The effect of the base to substrate ratio was investigated in this solvent. The rate of oxidation of 2,4-dinitrotoluene increased with increasing base concentration while that of TNT went through a maximum at a base to TNT ratio of about 0.75.

ESR experiments showed that 2,4-dinitrotoluene underwent electron transfer reactions in deficient base but not in the presence of excess base. No radicals were detected from TNT in excess or deficient base. Later workers found large quantities of radicals in the reaction of TNT with methoxide ion in DMSO-methanol mixture[30].

Oxidation of Aryl-Substituted Ethanes[54]

Bibenzyl did not undergo oxidation in 80/20 DMSO-t-butanol or 80/20 HMPA-t-butanol containing potassium t-butoxide. Tetraphenylethane, 1,2-bis (4-pyridyl) ethane and 1,2-bis (2-pyridyl) ethane oxidised to give the parent unsaturated compound, (eqn 12).

$$R_2CH - CHR_2 \xrightarrow[O_2]{\text{Base}} R_2C = CR_2 \qquad \text{(eqn 12)}$$

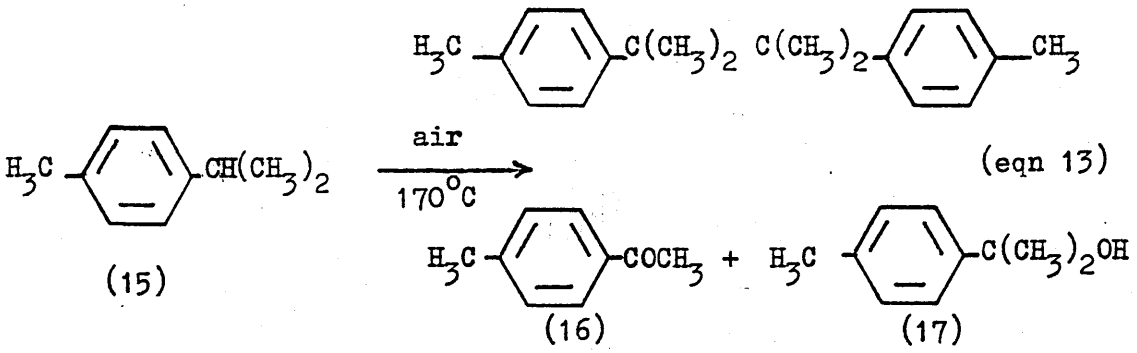
Low concentrations of paramagnetic substances were detected during these oxidations consistent with a radical type of oxidation.

3.1.3 Oxidative Coupling Reactions

An oxidative coupling reaction involves the combination of two molecules of a substance with the loss of two hydrogen atoms. Such reactions are often catalysed by a metal salt[55] but uncatalysed dimerisations are known.

Uncatalysed Oxidative Coupling

4-Nitrotoluene undergoes uncatalysed dimerisation to 4,4'-dinitrobibenzyl, this reaction was discussed above. 4-Cymene (15) couples on exposure to air at its reflux temperature [56], (eqn 13).



(15)

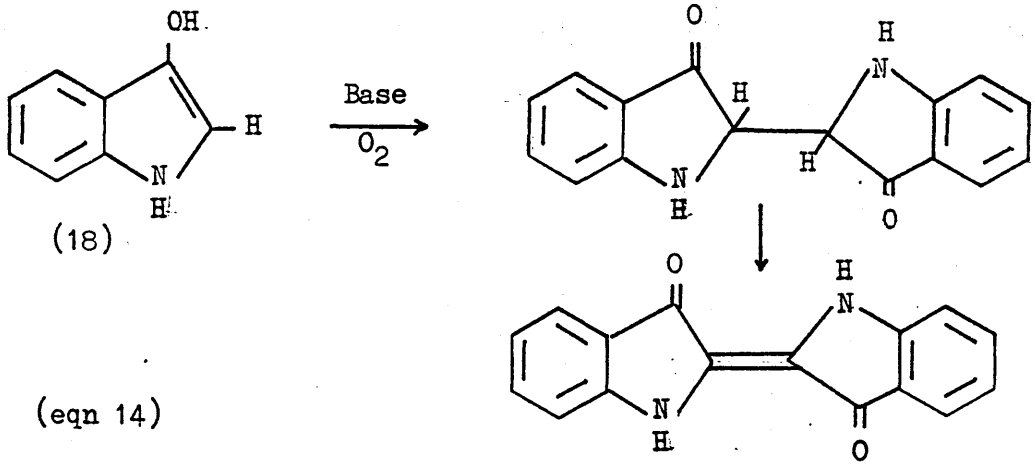
(16)

(17)

(eqn 13)

4-Acetyltoluene (16) and dimethyl-4-tolycarbinol(17) were also produced in appreciable quantities from this oxidation.

It has been shown that the reaction of indoxyl (18) with oxygen in basic solution to give indigo (20) involves leucoindigo (19) as an intermediate[57] (eqn 14).



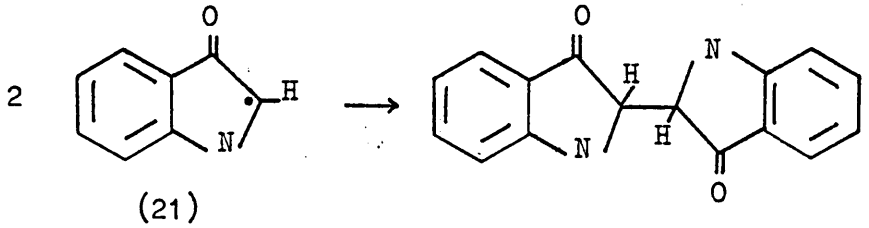
(18)

(19)

(20)

(eqn 14)

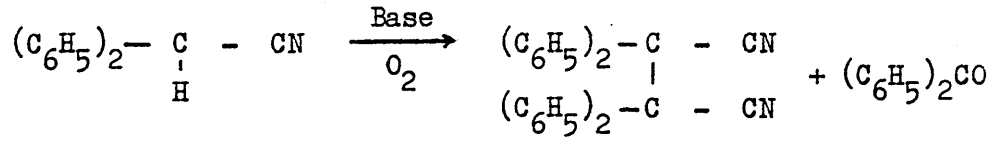
The most reasonable explanation for the formation of leucoindigo was thought to be the coupling of two indoxyl radicals (21, eqn 15).



(21)

(eqn 15)

A solution of diphenylacetonitrile (22) in piperidine containing sodium methoxide absorbed oxygen to give tetraphenylsuccinonitrile (23) in 20% yield and benzophenone (24) in 50% yield[58] (eqn 16).

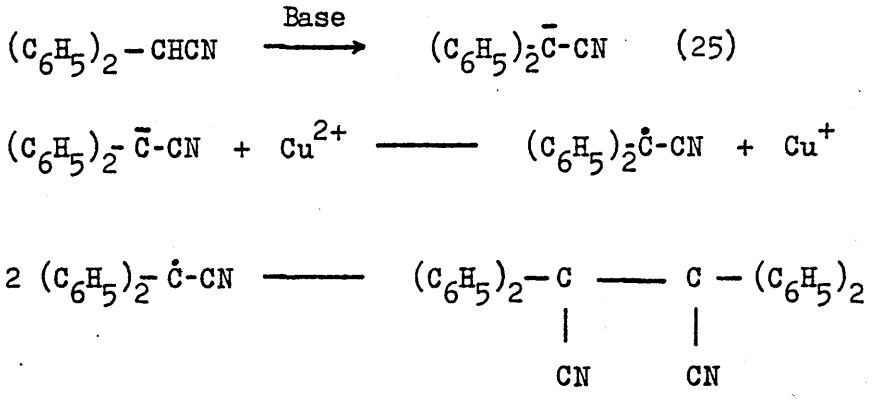


(22) (eqn 16) (23) (24)

Copper Catalysed Oxidative Coupling

The addition of a small amount of a copper salt to a solution of diphenylacetonitrile (22) in piperidine results in a considerable increase in the rate of oxygen absorption and an almost quantitative yield of the coupling product tetraphenylsuccinonitrile[58] (23).

Copper ions were thought to oxidise diphenylacetonitrile anions (25) to radicals which then coupled to give the observed product, (eqn 17).

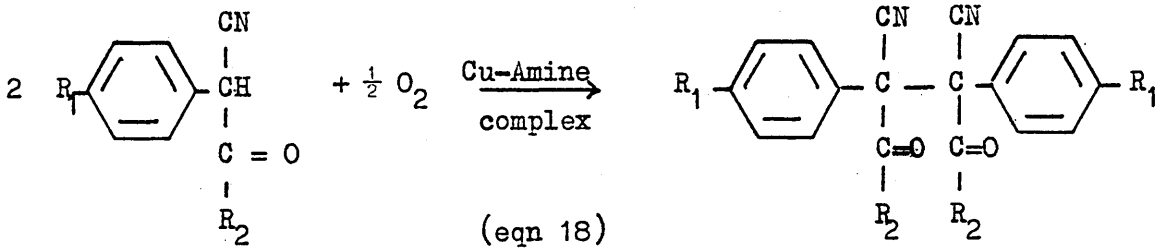


(eqn 17)

The role of oxygen was to regenerate the cupric ion.

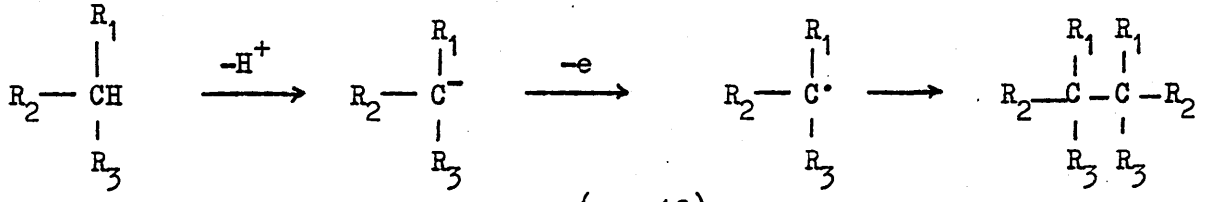
Other benzyl cyanides, α-substituted with an ester, acyl or amide group undergo oxidative coupling in a copper-amine-oxygen system

to give the carbon-carbon coupling products in high yield[59], (eqn 18).



(eqn 18)

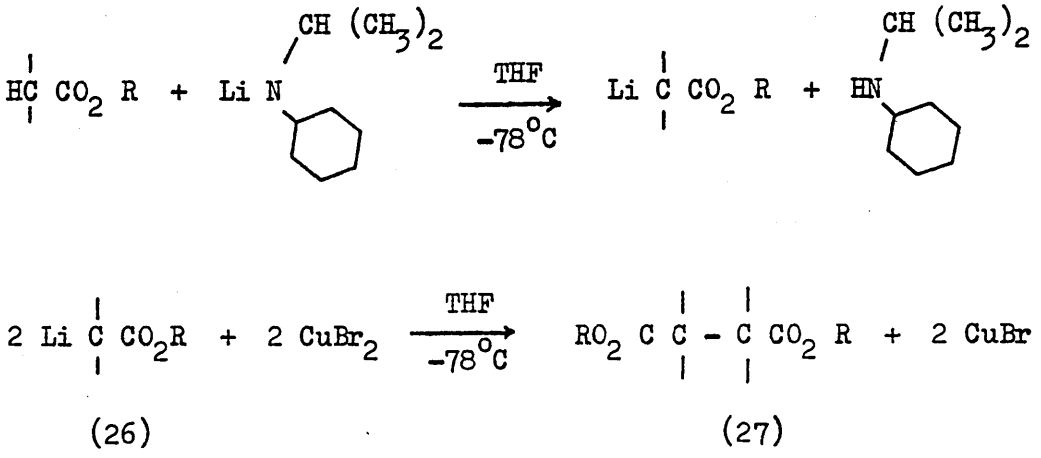
Again the mechanism proposed involved ionisation of the benzyl cyanide followed by electron transfer to cupric ions and then coupling of the resulting radicals, (eqn 19).



(eqn 19)

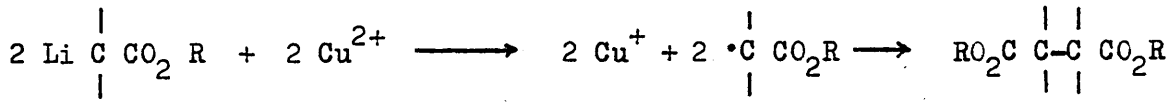
It was thought to be important that one of the groups R_1-R_3 should be able to complex with the copper catalyst. In this case that group was the nitrile group.

Ester enolates (26) dimerise in the presence of copper (II) salts to give substituted succinate esters (27) in reasonable yield[60], (eqn 20).



(eqn 20)

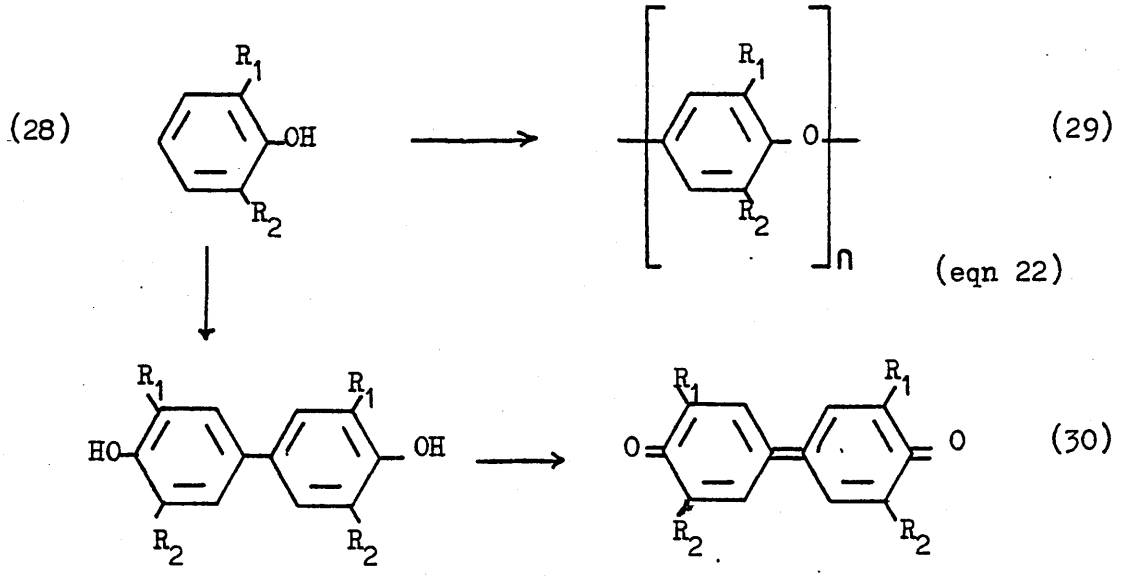
A radical-coupling mechanism accommodated the experimental results, (eqn 21).



(eqn 21)

A reaction which has received a great deal of study is the copper catalysed oxidative coupling of phenols. Interest has centred on this reaction not only because of its synthetic usefulness, but also because of its similarity to reactions of the copper oxidases[61].

As an example, 2,6-disubstituted phenols (28) undergo copper-amine catalysed oxidative coupling to give polymeric phenyl ethers (29) or diphenoquinones (30) depending on the constitution of the catalyst, (eqn 22).



(eqn 22)

The oxidative coupling reaction of 4-nitrotoluene to give 4,4'-dinitrobibenzyl is catalysed by copper-amine systems[62]. Acetylenes also undergo dimerisation in the presence of copper-amine mixtures[63].

3.2 Experimental Results and Discussion

At room temperature HNBB was the main product from oxidation of TNT by the Hungarian method, HNS being produced when the reaction mixture was warmed. With this in mind, the synthesis of HNS by the Hungarian method has been studied in two parts: firstly, the formation of HNBB from TNT and secondly, the conversion of HNBB to HNS.

The effects on both reactions of different bases, base concentration, various solvents and different catalysts were investigated. The rate of oxygen absorption was measured and some comparison made with the oxidation behaviour of 4-nitro- and 2,4-dinitrotoluene. The rates of reaction of TNT and formation of HNBB were investigated.

Results from this and the preceding chapter were used in a discussion of the mechanism of oxidation of TNT to HNBB and HNS. A comparison was made between the Hungarian and Shipp methods for the synthesis of HNS.

3.2.1 Oxidation of TNT to HNBB

3.2.1.1 Reaction Products

HNBB was the major product from catalysed and uncatalysed oxidations of TNT. However, there were significant differences between the product mixtures obtained from catalysed and uncatalysed reactions. Thin-layer chromatography (TLC), Fig. 3.1, showed that the crude product from uncatalysed oxidations contained at least five other, more polar components, in addition to TNT, HNBB and HNS. TLC of the crude product from oxidation of TNT in the presence of catalyst separated only three components, unreacted TNT, HNBB and HNS, leaving a brown material at the base of the TLC plate.

High performance liquid chromatography (HPLC) confirmed that a cleaner product was obtained from catalysed oxidation, Fig. 3.2. However, the HPLC results in Fig. 3.2. give a misleading picture of the purity of the crude product obtained directly from catalysed oxidation. Repeated recrystallisations were needed to free the product of the brown baseline

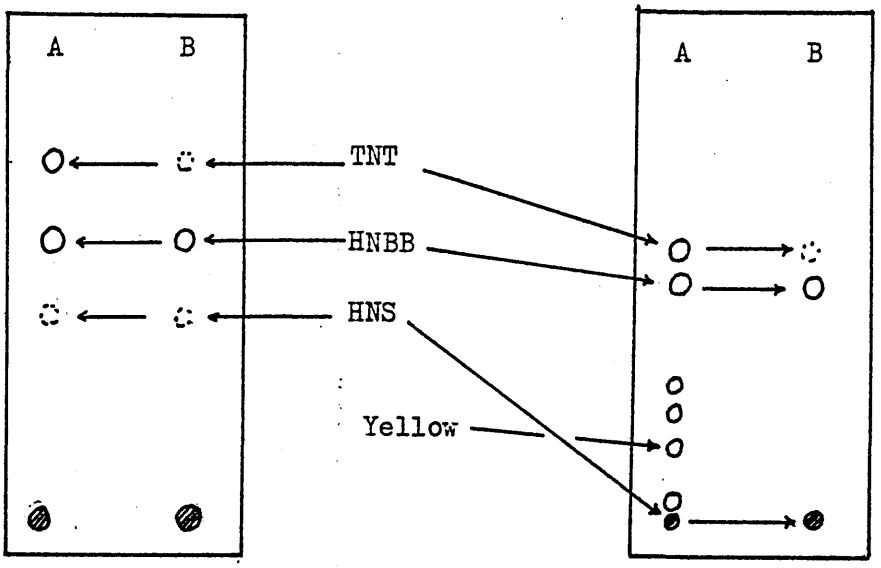


Fig. 3.1 TLC of crude reaction products; A, uncatalysed oxidation; B, catalysed oxidation.

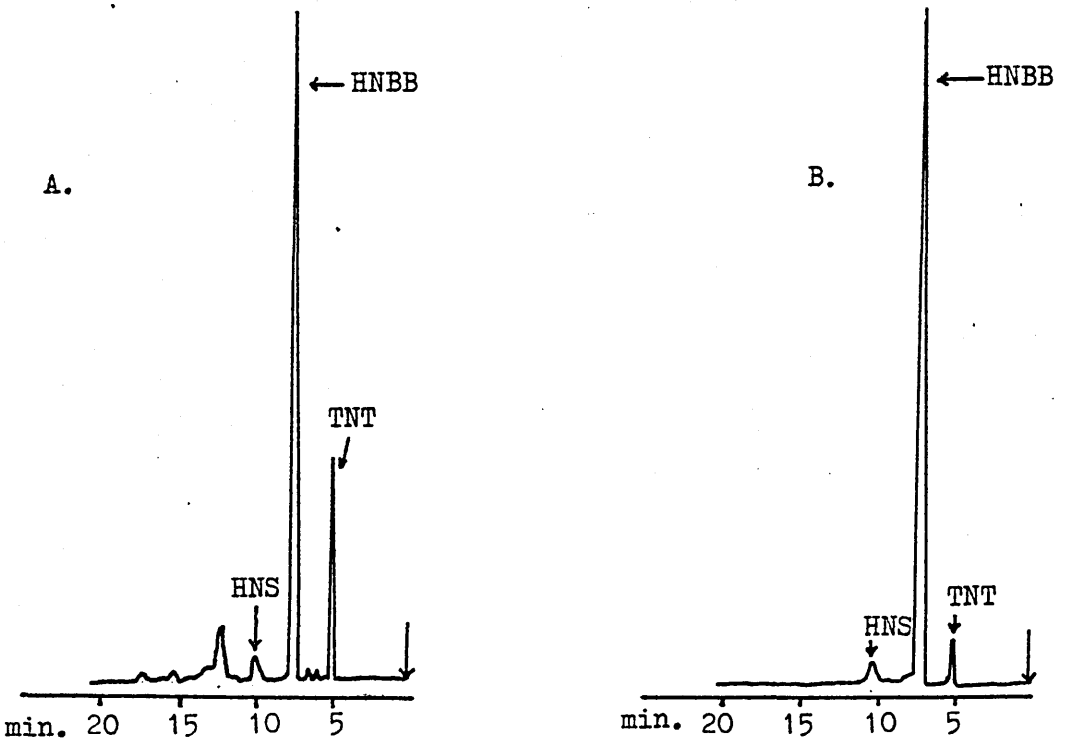


Fig. 3.2 HPLC of crude reaction products; A, uncatalysed oxidation; B, catalysed oxidation.

material mentioned above, which would be too polar to be eluted under the HPLC conditions used. None of the by-products of oxidation was present in sufficient concentration to allow identification of signals in the ^{1}HNMR spectra, other than those of TNT, HNBB and HNS.

All of the nitroaromatic compounds quickly oxidised to brown material on TLC plates left in air. When a solution of the crude reaction products came into contact with the silica of a chromatography column a deep red colour developed. A reaction between free hydroxyl groups in the silica and the nitroaromatics in the mixture was suspected of giving this colour. If the column was first washed with solvent containing a drop of acid, or prepared from acid-washed silica then this reaction did not occur.

An attempt was made to identify a yellow component which was observed during column chromatography of the crude products from uncatalysed oxidations but not in catalysed products. Short column chromatography using the better resolving power of TLC grade silica, was used to isolate a few mgs. of this material.

HNBB in the samples of crude products tailed badly during this chromatography and contaminated the yellow component of interest. It was not possible to rechromatograph the material because, once concentrated from the eluent, it quickly began to decompose.

This yellow component had a melting point of approximately 90^{o}C. Its infra-red spectrum was characteristic of a nitroaromatic compound, Fig. 3.3, and showed strong absorption at 1550 and 1360 cm^{-1} due to asymmetrical and symmetrical stretching of the N-O bonds in nitro groups. The stretching bands of the nitro group are very strong but it is not possible to estimate the number of nitro groups using these bands because of the variability of intensities from one compound to another.

The ^{1}HNMR spectrum of the yellow component Fig. 3.4, was contaminated by solvent peaks from residual undeuterated solvent and petrol eluent.

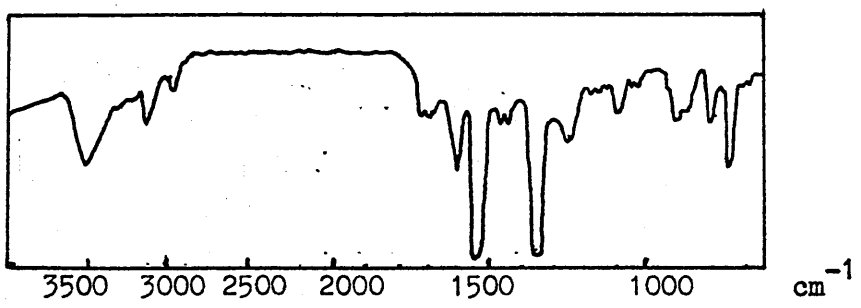


Fig. 3.3 Infra Red Spectrum of the yellow component.

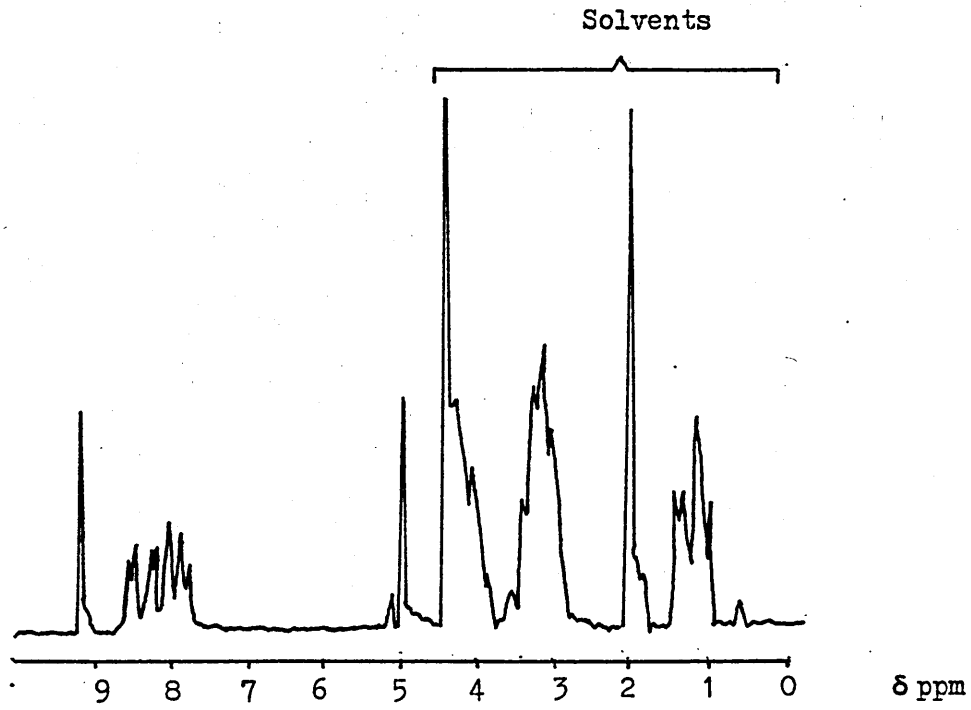
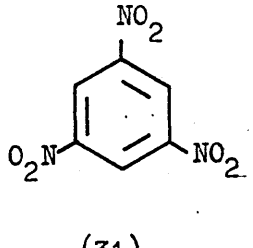


Fig. 3.4 ^{1}HNMR of the yellow component.

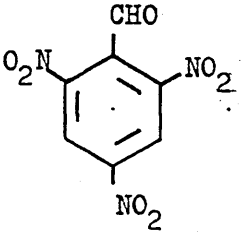
But it did show a multiplet centred around δ 8.2 ppm and a singlet at δ 5.0 ppm which did not arise from solvent or HNBB. Although the yellow component was known to be contaminated with HNBB, TLC suggested that not enough HNBB was present to give such an intense signal as was seen at δ 9.1 ppm. Assuming that the yellow component contributed to this signal then it too must contain a trinitroaromatic group.

The compound decomposed rather than fragmented in the mass spectrometer, shown by large peaks corresponding to oxygen and nitrogen in its mass spectrum.

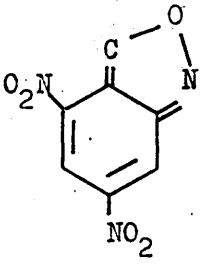
It is known that a large number of products can be formed from reactions involving TNT^- or σ-complexes as intermediates. Photolysis of TNT in aqueous solution[64] gave eight products which were identified as 1,3,5-trinitrobenzene (31), 2,4,6-trinitrobenzaldehyde (32), 4,6-dinitroanthranil (33), 2,4,6-trinitrobenzonitrile (34) and four isomers of tetranitroazoxytoluene (35).



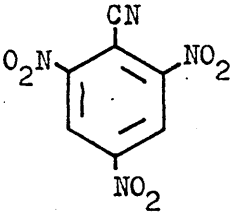
(31)



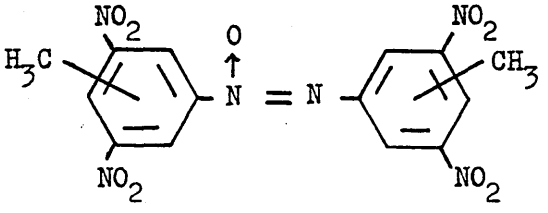
(32)



(33)

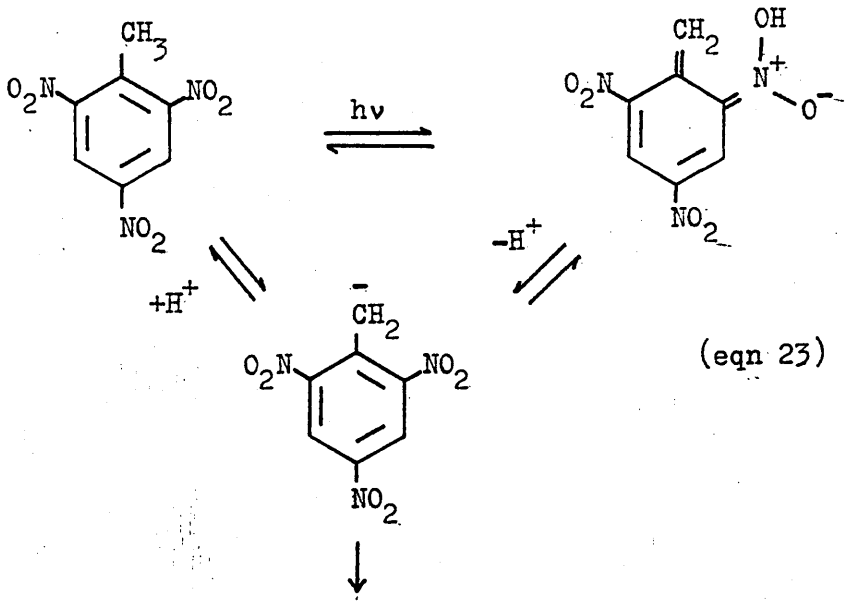


(34)



(35)

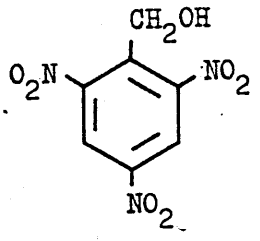
There is evidence that TNT^- is generated by irradiation of neutral and acidic aqueous solutions of TNT and that this is the precursor to the products described above[65]. The mechanism of ionisation was thought to involve aci-TNT (eqn 23).



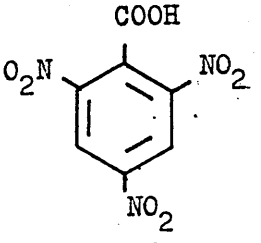
(eqn 23)

Decomposition Products

Thermochemical decomposition of TNT[66,67] was also thought to proceed via TNT^-. It yielded at least 25 products including 2,4,6-trinitrobenzyl alcohol (36), 2,4,6-trinitrobenzoic acid (37), 1,3,5-trinitrobenzene (31), 2,4,6-trinitrobenzaldehyde (32), 4,6-dinitroanthranil (33) and a large amount of an infusible telomeric or polymeric material of indefinite composition.

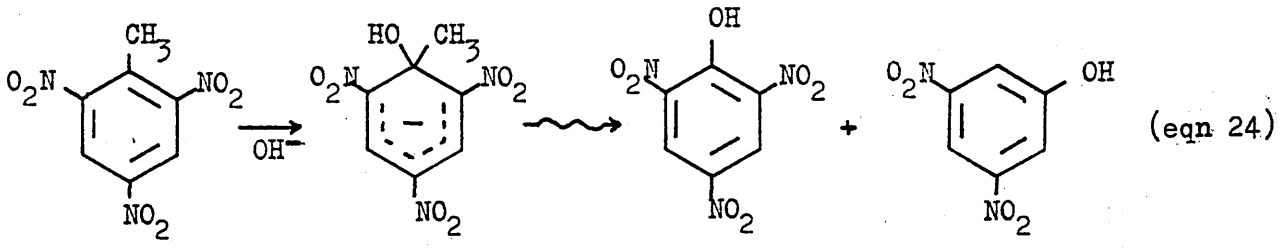


(36)



(37)

A σ-complex (38) was proposed as an intermediate in the formation of picric acid (39) and 2,4-dinitrophenol (40) from the reaction of TNT with hydroxide ions in aqueous solution [68], (eqn 24).



(38) (39) (40) (eqn 24)

Insufficient material and information was available for a structure to be assigned to this yellow component.

In order to assess the effect of reaction conditions on the oxidation of TNT to HNBB a routine method of analysis for HNBB was needed. The first method investigated made use of the intensely coloured σ-complexes formed between polynitroaromatic compounds and ethylene diamine (EDA)[41]. The nature of these complexes was discussed in Chapter 2.

The procedure adopted was similar to that already published in the literature[70]. It involved thin layer chromatography of a known weight of the crude reaction product using a silica plate and toluene as eluent. The plate was visualised under UV light, the zone containing HNBB marked then scraped from the plate. The HNBB zone was extracted with DMSO, EDA added to the extract and the absorbance of this solution measured. The concentration of HNBB present was obtained from a calibration curve.

This method, combining thin layer chromatography and visible spectrometry, although sufficiently accurate was too time consuming for routine use and an alternative was sought. In the ^{1}HNMR of crude reaction products the methylene signal from HNBB (δ 3.7 ppm) was well separated from signals due to TNT, HNS and other impurities. This signal was used as the basis

for quantitative NMR analysis of the reaction products using methylene chloride as an internal standard. The method had the great advantage that no separation procedure was necessary before the HNBB content could be assessed.

3.2.1.2 Base and Solvent Effects

Methanolic potassium hydroxide was the base used in all the examples in the Hungarian Patent to illustrate the process of oxidation of TNT. The effect on the yield of HNBB of using other bases is shown in Table 3.1. The best yield of HNBB was obtained from reactions in which one mole of base was present for every mole of TNT, Fig. 3.5.

At ratios of base to TNT of more than 1:1 the crude yield from the reaction dropped along with the amount of HNBB in the product. So as well as promoting the conversion of TNT to HNBB, base was involved in other reactions with TNT or HNBB or both, which yielded water soluble products.

From a thermodynamic standpoint, sodium hydride is a strong base but it reacted only slowly with TNT hence the low yield of HNBB.

The best yield of HNBB came from using sodium methoxide as base. Methanolic potassium hydroxide and tetramethylammonium hydroxide contain hydroxide ions which because of their smaller size are better nucleophiles than methoxide ions. These hydroxide ions may be involved in reactions to produce σ-complexes which lead to products other than HNBB, hence the lower yield.

A bulky, strong base such as potassium t-butoxide should readily ionise TNT but would be much less likely to become involved in the substitution reactions. Evidence of this is provided by a study of the reaction of TNT with potassium t-butoxide in t-butanol which concluded that the predominant reaction was proton abstraction and that the extent of σ-complex formation was small, if any[28]. The yield of

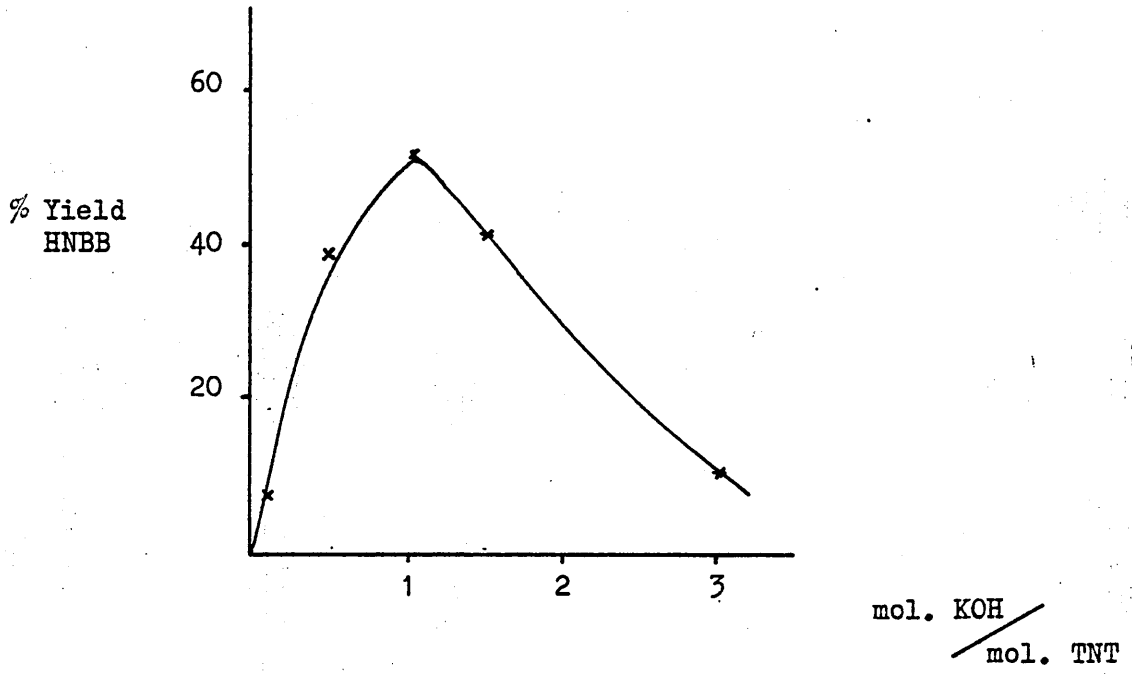


Fig. 3.5 Yield of HNBB as a function of potassium hydroxide concentration.

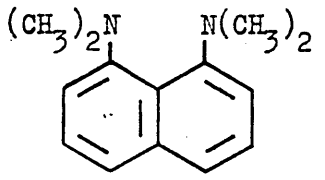
Table 3.1 Effect of different bases on the yield of HNBB

Base	% yield of HNBB
Methanolic potassium hydroxide	52
Sodium methoxide	82
Methanolic tetramethylammonium hydroxide	69
Potassium t-butoxide	10 [a]
Sodium hydride	21
1,8-bis-(N,N-dimethylamino)-napthalene	0

[a] product was mainly HNS

HNBB from reactions using potassium t-butoxide was small, around 10% of the theoretical yield, but the crude product did contain a relatively large amount of HNS, around 20% of theoretical. With other bases it was necessary to warm the reaction mixture to obtain any appreciable amount of HNS. This result was understandable in the light of the results of the spectroscopic investigation of the reaction of HNBB with potassium t-butoxide, described in Chapter 2. It was shown that the HNS radical anion was formed much more readily from HNBB using potassium t-butoxide than from reaction with methoxide ions. This was due to the reluctance of bulky t-butoxide ions to enter into σ-complex formation which was the preliminary interaction between HNBB and methoxide ions.

Another bulky base used in the reaction was 1,8-bis-(N,N-dimethyl-amino)-napthalene or 'proton sponge' (41).



(41)

The steric strain in this molecule is relieved on protonation which makes 'proton sponge' a very strong base compared to other amines. Although a relatively strong base the molecule is a poor nucleophile because of steric reasons. However, proton sponge is not as strong a base as the oxygen bases used and although some ionisation of TNT occurred, shown by the purple colour of the reaction solution, most of the TNT was recovered from the reaction, unchanged.

Four different kinds of solvent can be recognised[71]. Proton donating solvents, similar in many ways to water, such as the lower alcohols and polyols; proton donating, non-polar solvents such as the butanols and aniline; non-proton donating polar solvents such as

dimethylformamide and dimethylsulphoxide; non-proton donating, non-polar solvents such as tetrahydrofuran, diethyl ether and dioxane. The oxidation of TNT to HNBB went well in non-proton donating or aprotic, polar solvents such as dimethylformamide, Table 3,2.

There are also four kinds of strong solvent-solute interaction: ion-dipole; dipole-dipole; π-complex-forming and hydrogen bonding. In protic solvents such as water and alcohols, ions are solvated by ion-dipole interaction on which is superimposed a strong hydrogen-bonding. In polar, aprotic solvents such as DMF ions are solvated by ion-dipole interactions in which there is superimposed an interaction due to the mutual polarisability of the ion and solvent molecule. There is no significant contribution from hydrogen-bonding in aprotic solvents.

Polar aprotic solvents are found to solvate cations most strongly and leave anions relatively unencumbered and highly reactive. Large polarisable anions are however, more solvated in aprotic solvents because of the large interaction due to mutual polarisability of solvent and solute.

Thus, the oxidation of TNT to HNBB went well in polar aprotic solvents for two reasons: (i) ionisation of TNT was promoted by good solvation of the large TNT anion; and, (ii) hydroxide and methoxide ions due to the lack of hydrogen bonding are much less solvated than in aqueous media, and are thus highly reactive in these solvents.

Table 3.2 Effect of different solvents on the yield of HNBB

Solvent	% Yield HNBB	Catalyst
A. Patent Examples		
dimethylformamide	37	-
dimethylacetamide	44	-
dimethylsulphoxide	38	-
N-methylpyrolidone	34	-
pyridine	25	-
tetrahydrofuran	18	-
triglyme	6	-
ethyl acetate	2	-
50/50 tetrahydrofuran-dimethylacetamide	82	copper sulphate-pyridine
B. Experimental Results		
dimethylformamide	52	copper sulphate-pyridine
tetrahydrofuran	10	copper sulphate-pyridine
toluene	0	copper sulphate-pyridine

3.2.1.3 Oxygen

Some HNBB was formed from reactions carried out under a nitrogen atmosphere. Even using carefully deoxygenated solutions the yield of HNBB was still around 15% of the theoretical yield. However, oxygen was vital to obtaining a good yield of HNBB. That oxygen was consumed during the oxidation of TNT to HNBB was shown in a series of experiments using the apparatus shown in Fig. 3.6.

The apparatus was filled with oxygen and reaction started by mixing the contents of the sidearm with those of the flask. Oxygen uptake was followed at atmospheric pressure by manually keeping the water in the two arms of the manometer at the same level. Careful control of reaction conditions, in particular temperature and the rate of stirring, enabled reproducible results to be obtained from this apparatus for the oxygen uptake from basic solutions of TNT and other nitroaromatic compounds.

Oxygen uptake curves from TNT in basic solution are shown in Fig. 3.7. Less oxygen was absorbed in the presence of the copper sulphate-pyridine additive and no oxygen uptake occurred in the presence of ferric chloride. The purple colour of the reaction mixture in this last case showed that ionisation of TNT had occurred but unreacted TNT was all that was recovered at the end of the reaction time.

The oxidation of 4-nitrotoluene in basic solution has some resemblance to the oxidation of TNT in yielding 4,4^{1}-dinitrobibenzyl and 4,4^{1}-dinitrostilbene, along with some 4-nitrobenzoic acid (eqn 8). If a mechanism similar to that which is favoured for oxidation of 4-nitrotoluene, (eqn 10), is used to rationalise the oxidation of TNT this would explain why the formation of HNBB was so sensitive to the presence of oxygen, which is acting as an electron acceptor. Some HNBB was formed in the absence of oxygen because the TNT molecule itself can act as an electron acceptor[40].

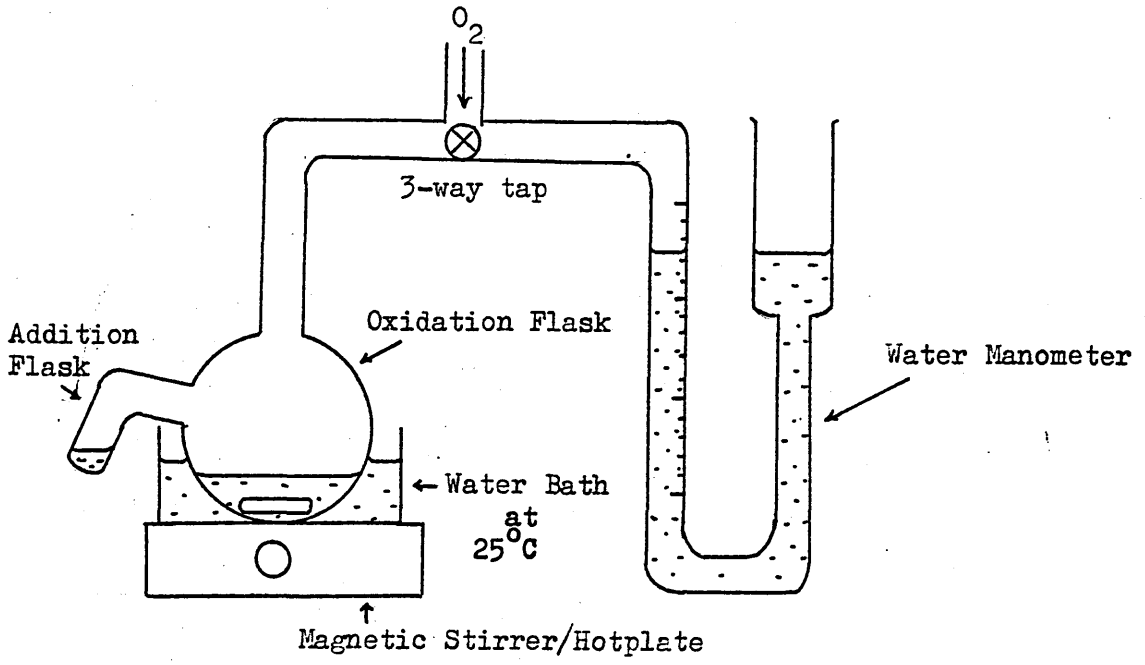


Fig. 3.6 Oxidation Apparatus.

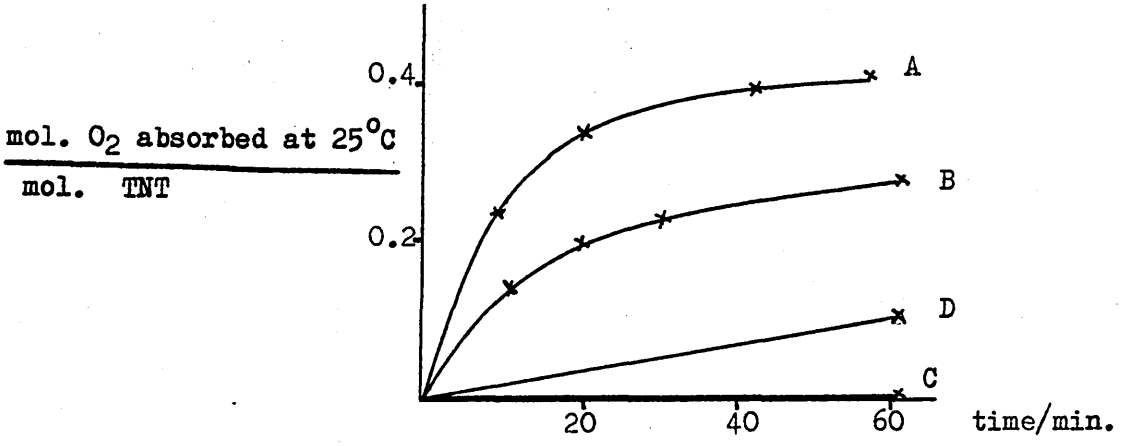
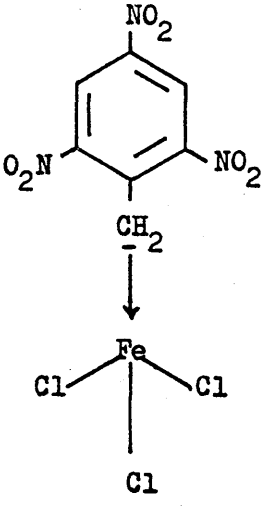


Fig. 3.7 Oxidation of TNT (2×10^{-1} mol.dm.$^{-3}$) in the presence of potassium hydroxide (1.7×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol: A, no catalyst; B, copper sulphate-pyridine catalyst; C, ferric chloride catalyst.
D, TNT (1.1×10^{-1} mol.dm.$^{-3}$), potassium t-butoxide (3.9×10^{-1} mol.dm.$^{-3}$) in t-butanol[14].

The reaction was improved by the addition of cupric ions which readily promote electron transfer reactions, being reduced to cuprous ions in the process. The role of oxygen might then be the oxidation of cuprous ions back to cupric ions. In the presence of cupric ions the number of moles of oxygen absorbed was roughly equivalent to the number of moles of copper present.

The importance of polar aprotic solvents in oxidation of TNT was again seen on comparing the rate of oxidation in DMF with that published for the reaction in t-butanol[14], Fig. 3.7.D. No dimers were isolated from the oxidation in t-butanol.

In the absence of catalyst, TNT reacts to form some HNBB. However, the addition of ferric chloride to an oxidation reaction mixture only resulted in TNT being recovered at the end of the reaction time. Ionisation of TNT did occur because the intense purple colour of the trinitrobenzyl carbanion was seen. Ferric chloride, a Lewis acid, could stabilise the TNT anion and prevent further reaction (42).



(42)

3.2.1.4 The Rate of Reaction

Many quantitative data are now available concerning the rate of reaction of TNT in basic solution[26,27,28,34]. Most of these studies involved the use of stopped-flow spectrophotometry on dilute solutions under pseudo-first order reaction conditions.

By using the greater diagnostic ability of ^{1}HNMR it was hoped to carry out an experiment to measure the rate of reaction of TNT in basic solution, the rate of appearance and disappearance of intermediates and the rate at which HNBB was formed, under a variety of conditions. Although potentially more information can be gained from a ^{1}HNMR spectrum the technique lacks the sensitivity of spectrophotometry and much more concentrated solutions of reactants are needed.

On mixing TNT and potassium hydroxide in a deuterated dimethyl-sulphoxide-methanol mixture, the resonance signals due to TNT protons disappeared and were replaced by weak, broad signals which changed over the time period studied. The reasons for this behaviour were discussed in Chapter 2 but such spectra were of little use in quantifying the extent of reaction.

Some information on rate of reaction was gained by removing aliquots from a reaction mixture, quenching the reaction by running the aliquots into acidified water and then analysing the resulting precipitates by quantitative ^{1}HNMR using an internal standard. The results of such experiments are shown in Fig. 3.8 A-C.

The results did not fit any simple rate law. The rate of disappearance of TNT in all the cases was similar and reflected the rate of ionisation. The concentration of HNBB reached a maximum and then began to decrease in the uncatalysed reaction, whilst in the presence of copper ions the HNBB concentration reached a steady value. This result suggested that the catalyst might be acting to stabilise the product of the reaction, possibly by complexation or the inhibition of side reactions. Little HNBB was

(A)

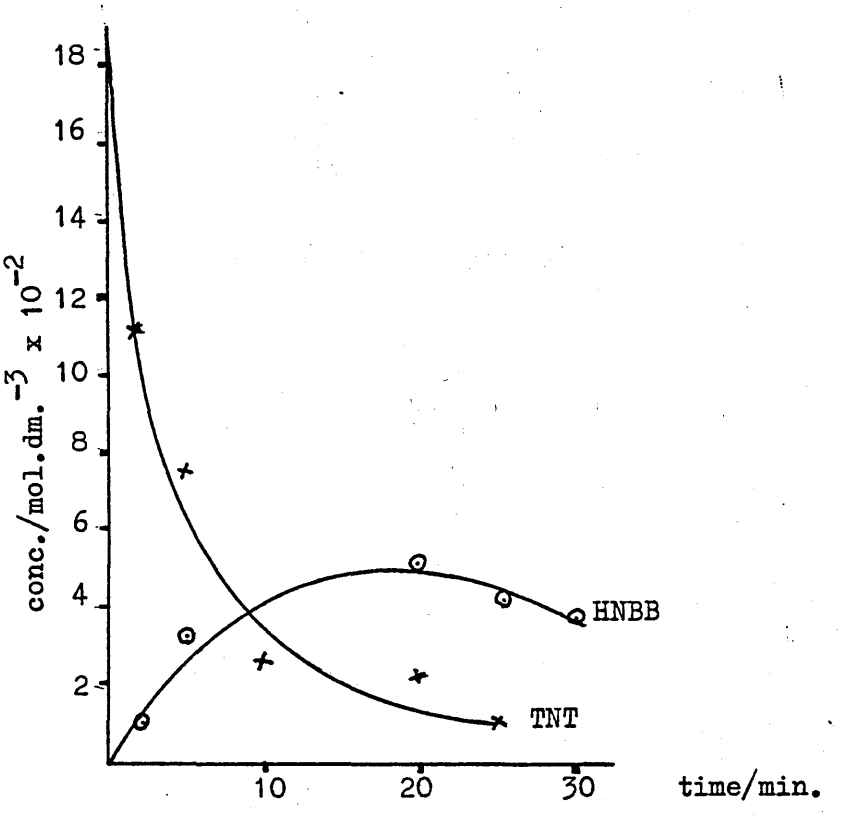


Fig. 3.8.A. Rate of reaction: TNT (1.8×10^{-1} mol.dm.$^{-3}$), potassium hydroxide (1.9×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol, oxygen atmosphere.

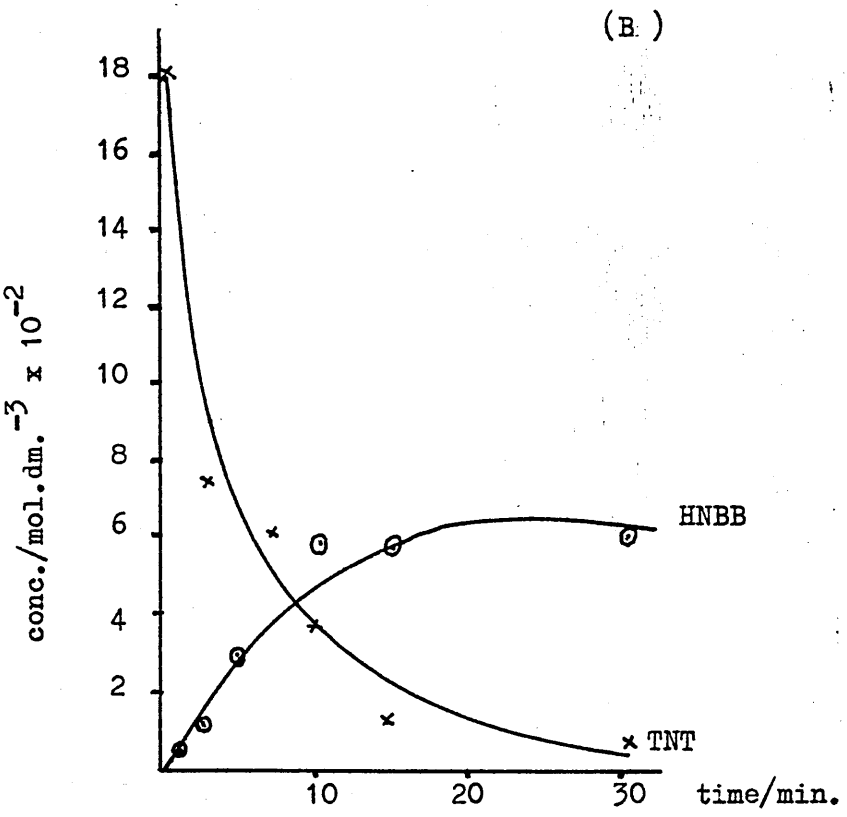


Fig 3.8.B. Rate of reaction: TNT (1.8×10^{-1} mol.dm.$^{-3}$), potassium hydroxide (1.9×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol, oxygen atmosphere, copper sulphate-pyridine catalyst.

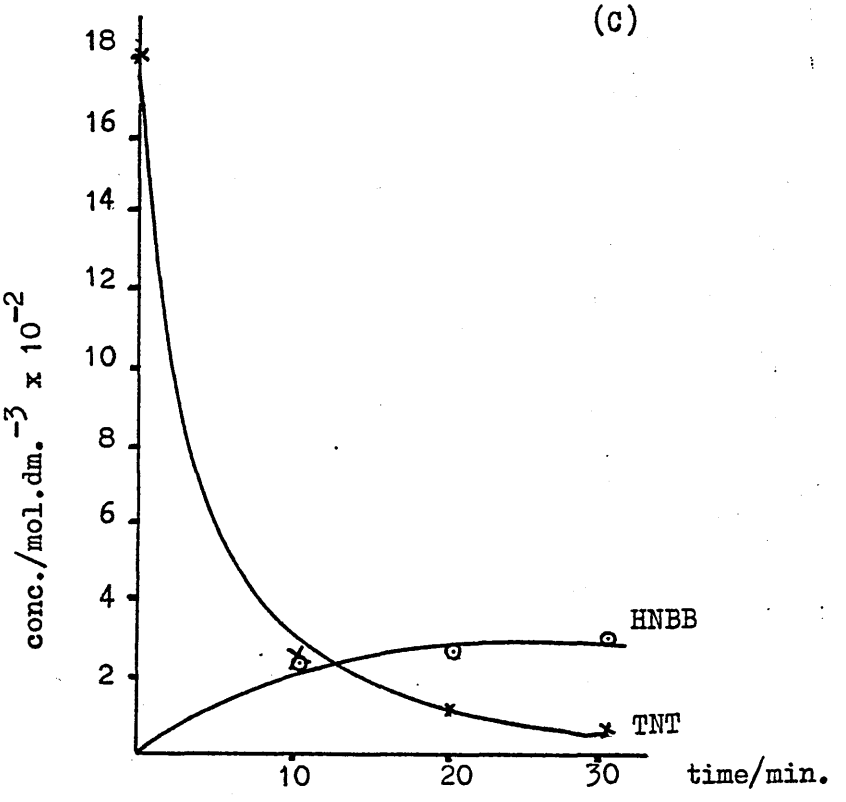


Fig 3.8.C. Rate of reaction: TNT (1.8×10^{-1} mol.dm.$^{-3}$), potassium hydroxide (1.9×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol, nitrogen atmosphere.

formed from reactions under nitrogen, the main product from which was a red material of unknown composition. This material also contaminated the products from reactions in the presence of oxygen but to a lesser extent.

Crude quantitative data were thus obtained from these experiments but perhaps the most useful information would come from a study of the rate of disappearance of TNT^-. This would require the use of one of the methods of investigating fast reactions and was beyond the scope of this present work.

3.2.1.5 Catalysts

A catalyst is a substance that increases the rate of reaction when present in small amounts. It is unchanged chemically at the end of the reaction, although it may participate in the reaction and be subsequently regenerated.

The catalyst used in the Hungarian Patent was a slurry of copper sulphate in pyridine. The choice of this catalyst might have been influenced by the fact that copper compounds catalyse an exceeding array of reactions in organic solvents[72] including many oxidative coupling reactions[58,59,60,61]. In particular the oxidative coupling of 4-nitrotoluene to 4,4'-dinitrobibenzyl and 4,4'-dinitrostilbene is catalysed by mixtures of copper II salts with amines[62].

The effect of the copper sulphate-pyridine slurry and other catalysts on the yield of HNBB from the oxidation of TNT has been investigated and the results are presented in Table 3.3.

A relatively large amount of copper compound was needed to have an effect on the reaction. At less than 0.1 mole of copper for each mole of TNT the yield of HNBB was not much improved. Copper sulphate is only slightly soluble in DMF and although a large amount of copper compound was needed to have an effect on the reaction only a small amount of this

Table 3.3 Effect of different catalysts on the yield of HNBB

Catalyst	mol Cu/mol TNT	% yield HNBB
none	-	34
$CuSO_4$-pyridine slurry	0.03	32
$CuSO_4$-pyridine slurry	0.15	52
$CuSO_4$-pyridine slurry	0.30	52
$CuSO_4$-pyridine slurry	0.60	48
$CuSO_4$-pyridine filtrate	-	40
$CuSO_4 5H_2O$-pyridine slurry	0.20	43
$CuSO_4$	0.30	19
$CuSO_4$ in solution in DMF	0.13	66
$CuSO_4$-DMF solution + pyridine	0.13	64
Ppt. from reaction of $CuSO_4$-DMF solution with KOH	0.13	76
Filtrate from reaction of $CuSO_4$-DMF solution with KOH	-	41
$CuSO_4$-DMF-KOH ppt. under N_2	1.00	29
$CuCl_2$-pyridine	0.37	24
CuCl-pyridine	0.50	50
$[Cu(pyridine)_2](SCN)_2$	0.15	41
$[FeCl_3$ 6.3×10^{-4} mol.	19°C and 31°C	unreacted TNT recovered$]$

copper was in solution. Copper sulphate alone gave a low yield of HNBB which suggested that pyridine was important for getting copper ions into solution by complexing them. However, the filtrate from a copper sulphate-pyridine slurry did not improve the yield of HNBB as much as the original slurry.

The Hungarian Patent also gives examples of the use of cobalt naphthenate as an alternative oxidation catalyst. Other catalysts that have been investigated at PERME include salts of manganese, antimony, rhodium and molybdenum[73]. Most improved the reaction more or less but for ease of preparation and then removal at the end of reaction, the copper sulphate-pyridine slurry was preferred. The biggest drawback with this system was that it was not very soluble in the reaction solvent. This did not help in understanding what was the active catalytic species and how much was present in the reaction mixture.

Other copper II compounds such as copper II chloride and the complex, $[Cu(pyridine)_2](SCN)_2$ were soluble in the reaction solvent but did not function very well as catalysts for the reaction. In contrast, a soluble catalyst prepared from copper I chloride in pyridine was active in the reaction and gave a good yield of HNBB. Similar behaviour was reported in the copper catalysed oxidative coupling of phenols where a copper II complex prepared by oxidation of copper I chloride in pyridine with oxygen was active in the reaction but many simple copper II salts were not[61].

The formation of the active catalyst could involve a reaction between the copper species present in solution and the base used to ionise TNT. Copper sulphate slowly dissolved in DMF to give a green solution which improved the yield of HNBB from oxidation of TNT. The addition of methanolic potassium hydroxide to this solution gave a green-brown gelatinous precipitate. This was filtered off and found to give a good yield of HNBB when added to the oxidation reaction mixture. The filtrate

had no effect on the oxidation reaction.

The visible spectrum of a mixture of copper sulphate and pyridine in DMF, Fig. 3.9.A, was that expected for a copper complex[74]. The absorption band at about 680 nm gave the solution its blue colour with a strong ultra-violet band due to charge-transfer. The addition of base, Fig. 3.9.B, decreased the intensity of the longer wavelength band but the charge-transfer band now tailed into the blue end of the spectrum causing the brown colour of the solution.

The only strong features in the infra-red spectrum of the green-brown precipitate, Fig. 3.10, were an O-H stretching band at 3500 cm^{-1} and a sulphate band at 1130 cm^{-1} [75].

The exact structure of the active catalyst in copper catalysed oxidative coupling reactions is still under investigation[76,77,78]. However, the heart of the mechanism of catalysis in many of these reactions is believed to be electron transfer from a carbanion to a copper II ion.

The trinitrobenzyl carbanion is highly resonance stabilised and will not normally undergo ready electron transfer[54]. Some oxidation of the carbanion does occur through electron transfer reactions with oxygen or in the absence of oxygen with unionised TNT, but the success of the Hungarian Patent is, that by the addition of a metal catalyst, the rate of electron transfer has been increased and the subsequent yield of HNBB improved.

In the absence of catalyst, TNT reacts to form some HNBB for reasons outlined above. However, the addition of ferric chloride to an oxidation reaction mixture only resulted in TNT being recovered at the end of the reaction time. Ionisation of TNT did occur because the intense purple colour of the trinitrobenzyl carbanion was seen. As suggested earlier, ferric chloride, a Lewis acid, could stabilise the TNT anion and prevent further reaction.

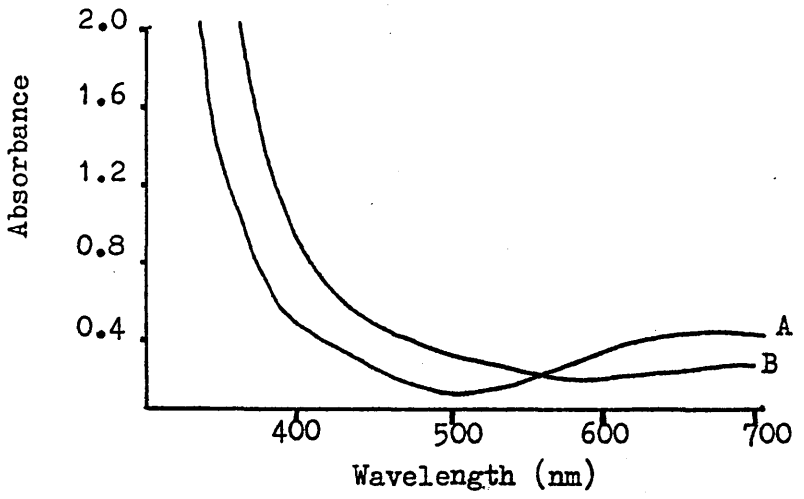


Fig. 3.9. Visible spectra: A, a solution of copper sulphate and pyridine in DMF; B, the same solution after the addition of methanolic potassium hydroxide.

Fig. 3.10. Infra-Red spectrum of the green-brown precipitate

3.2.2 Oxidation of HNBB to HNS

A basic solution of HNBB, in a polar aprotic solvent such as DMF, on warming to around 55°C yielded HNS as the main product. The effect of different conditions on the reaction is shown in Table 3.4.

The addition of a copper sulphate-pyridine slurry greatly improved the yield of HNS, just as the yield of HNBB from oxidation of TNT had been improved. The effect of catalyst suggested that both the oxidation of TNT to HNBB and the formation of HNS from HNBB, proceeded by similar mechanisms and that electron transfer was an important step.

Again, as with the synthesis of HNBB, a much cleaner product was obtained from catalysed reactions, Fig. 3.11. The crude products from uncatalysed reactions had present at least six components more polar than HNBB, whereas the products from catalysed reactions only comprised brown baseline material along with HNS. The unwanted by-products did not pose as much a problem as the by-products from the oxidation of TNT. The low solubility of HNS in common organic solvents meant that the crude product could be washed with acetone to remove the contaminants.

The synthesis of HNS from HNBB did contrast, in some ways, with the oxidation of TNT to HNBB, despite the similarity of the effect of catalyst. In the first place much less base was needed to effect the transformation. Only one mole of base was used for every five moles of HNBB. Higher or lower ratios decreased the yield of HNS. Secondly, the reaction did not require the presence of oxygen. A good yield of HNS was obtained from catalytic reactions carried out under nitrogen.

The oxygen uptake curve from a basic solution of HNBB at 20°C is shown in Fig. 3.12. Oxygen absorption only began after a 30 min. induction period during which the colour of the reaction solution changed from red-brown to blue.

Table 3.4 Effect of different conditions on the oxidation of HNBB to HNS

mol HNBB/mol KOH	Catalyst	% yield HNS
5	-	39
5	$CuSO_4$-pyridine	74
5	$CuSO_4$-pyridine/N_2 atm.	73
50	$CuSO_4$-pyridine	20
1	$CuSO_4$-pyridine	26

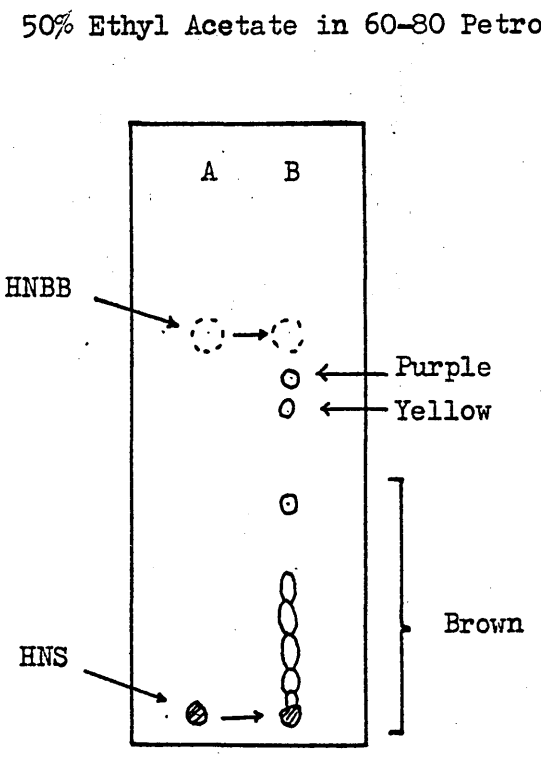


Fig. 3.11. TLC of crude reaction products; A, catalysed oxidation of HNBB; B, uncatalysed oxidation of HNBB.

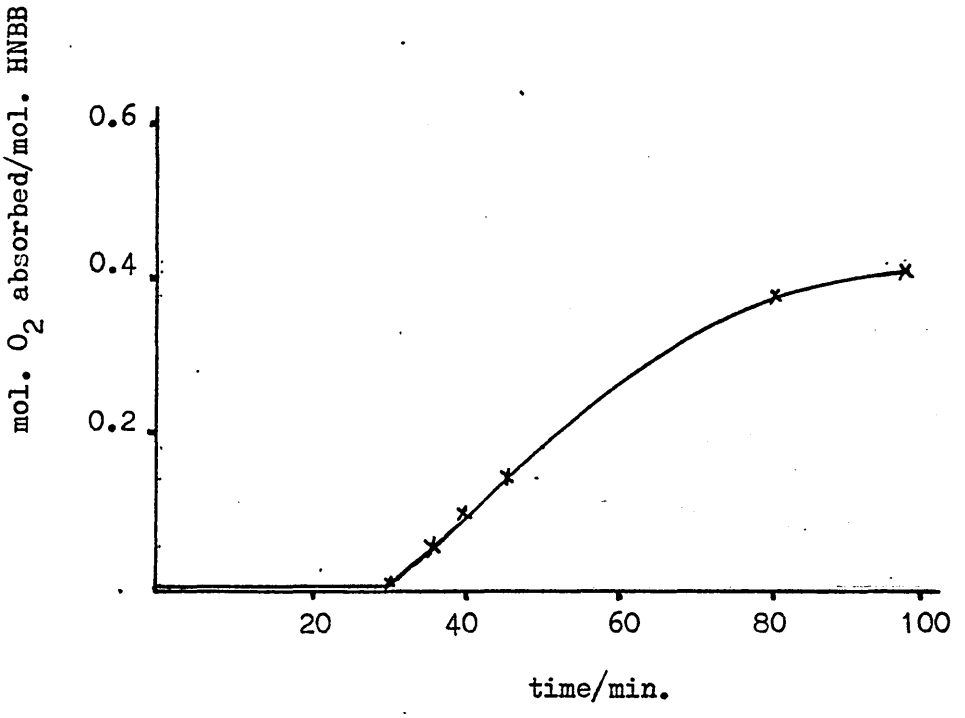


Fig. 3.12. Oxidation of HNBB (5×10^{-2} mol.dm.$^{-3}$) in the presence of potassium hydroxide (5×10^{-2} mol.dm.$^{-3}$) in 97/3 DMF-methanol.

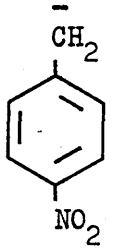
The oxidation of HNBB to HNS was thus improved by a copper catalyst but contrasted with the oxidation of TNT in using less base and in the effect of oxygen.

3.2.3 Oxidation of 4-Nitrotoluene and 2,4-Dinitrotoluene

In the early stages of this research programme the effect of the Hungarian Patent reaction conditions on 4-nitro- and 2,4-dinitrotoluene was investigated. Similarities between the behaviour of these compounds and TNT would enable these less hazardous materials to be used as model compounds to gain information about reactions of nitroaromatic compounds under the conditions of interest.

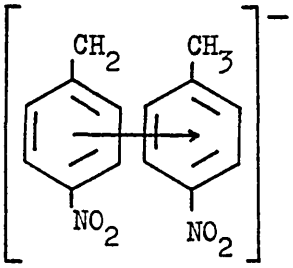
Both 4-nitro- and 2,4-dinitrotoluene gave rise to intense colours in basic solution. A solution of 4-nitrotoluene in DMF went yellow immediately after adding base and over the next few minutes changed through green to deep blue-black. 2,4-Dinitrotoluene in DMF gave a green colour in basic solution. The initial colours from 4-nitrotoluene proved too transient to be recorded on a conventional spectrophotometer. The spectra in Fig. 3.13 are those of the deep blue-black from 4-nitrotoluene and the green from 2,4-dinitrotoluene in the presence of base.

When 4-nitrotoluene in t-butanol was treated with potassium t-butoxide a yellow colour developed[38]. After a short period of time the colour changed to blood-red and at about the same time an ESR signal became detectable. The yellow colour was attributed to the 4-nitrobenzyl anion (43) and the red product to the 4-nitrotoluene radical anion (44).

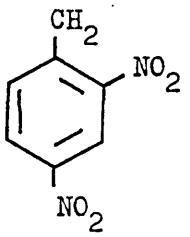


(43)

(44)



(45)



(46)

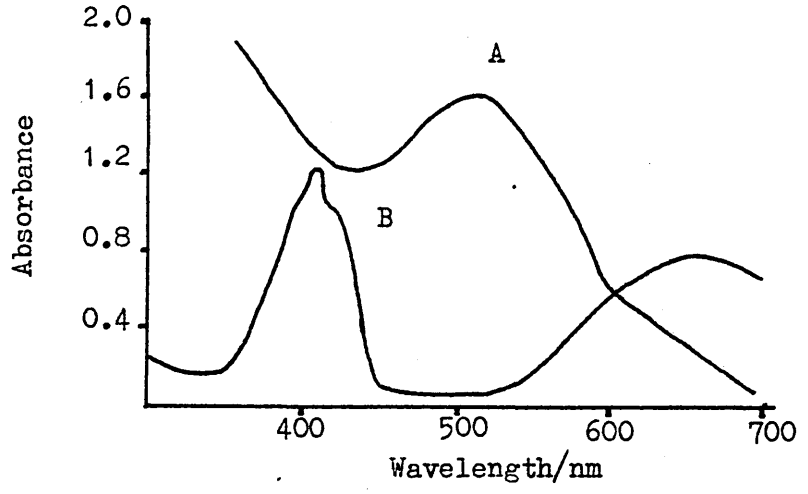


Fig. 3.13 . Visible spectra: A, 4-nitrotoluene ($2{,}5 \times 10^{-4}$ mol.dm^{-3}) in the presence of potassium hydroxide (1.7×10^{-2} mol.dm^{-3}) in 99/1 DMF-methanol; B, 2,4-dinitrotoluene (2.2×10^{-4} mol.dm^{-3}), potassium hydroxide (8×10^{-4} mol.dm.$^{-3}$) in 99/1 DMF-methanol.

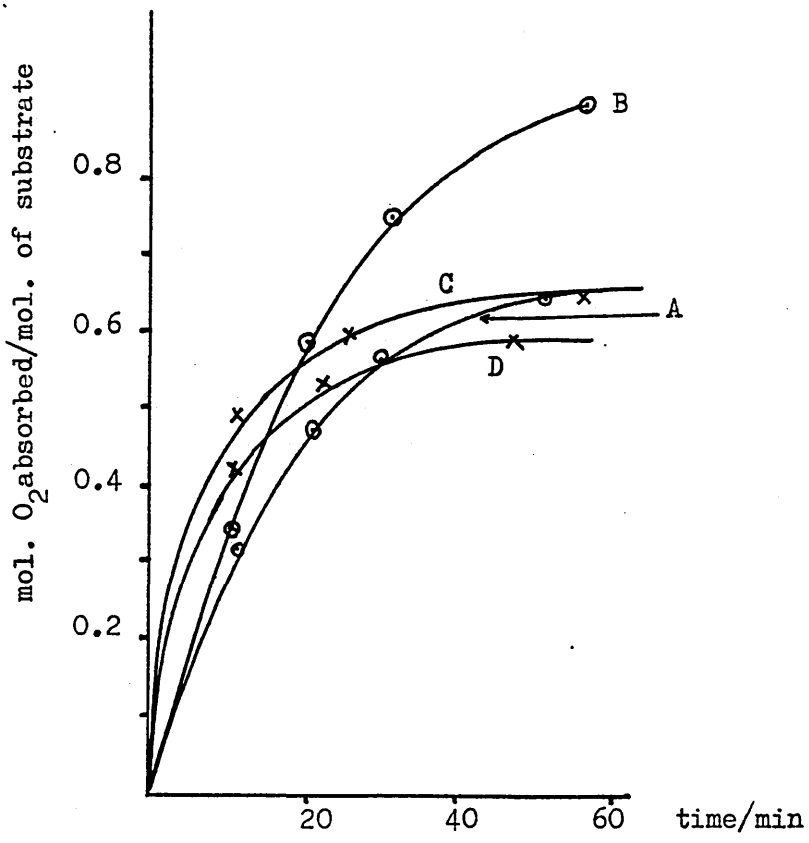
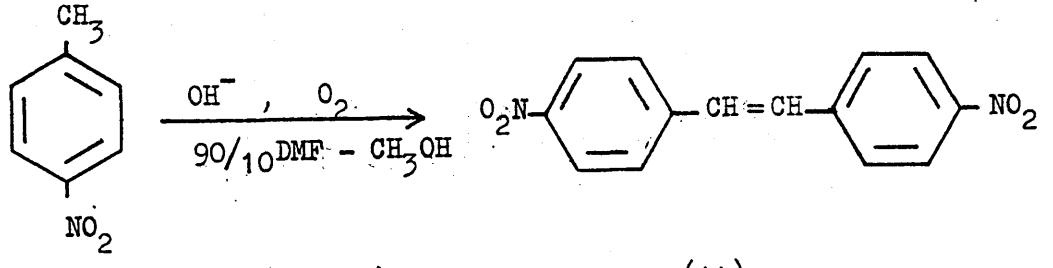


Fig. 3.14. Oxygen uptake in the presence of potassium hydroxide (1.7×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF-methanol: A, 4-nitrotoluene; B, 4-nitrotoluene and copper sulphate-pyridine catalyst; C, 2,4-dinitrotoluene; D, 2,4-dinitrotoluene and catalyst; all 2×10^{-1} mol.dm.$^{-3}$

It was also noted that in dimethyl sulphoxide solution, wherein the radical build up was expected to be more rapid, the radical-ion appeared green-blue. This suggested that the species responsible for the spectrum in Fig. 3.13.A was the radical anion of 4-nitrotoluene. However, there was also evidence that absorption due to the formation of a charge-transfer complex (45) also contributed to the colour of basic solutions of 4-nitrotoluene[52].

The spectrum observed from 2,4-dinitrotoluene in basic DMF, Fig. 3.13.B, was similar to that attributed to the 2,4-dinitrobenzyl anion (46)[79]. But again there was evidence that the reaction was more complex, ESR experiments showed that 2,4-dinitrotoluene underwent electron transfer reactions in deficient base but not in the presence of excess base[39].

Under conditions similar to those used to convert TNT to HNBB, 4-nitrotoluene yielded 4,4'-dinitrostilbene (11) as the predominant reaction product, (eqn 25).



(eqn 25) (11)

The yield of stilbene was about doubled in the presence of copper sulphate-pyridine catalyst, from around 20% of theoretical to over 40% yield. Oxidation of 2,4-dinitrotoluene gave a complicated brown mixture

in which no one product predominated.

Oxygen uptake curves from 4-nitro- and 2,4-dinitrotoluene are shown in Fig. 3.14. Solutions of 4-nitrotoluene in the presence of base absorbed oxygen more quickly than similar solutions of TNT, Fig. 3.7. The effect of adding copper sulphate-pyridine catalyst was to increase the rate of oxygen uptake in contrast to the result obtained with TNT. Basic solutions of 2,4-dinitrotoluene took up oxygen more quickly than similar solutions of 4-nitrotoluene but adding catalyst had little effect on the rate of oxygen absorption.

The explanation for the different oxidation behaviour of the three nitrotoluenes probably lies in the relative acidities of the compounds, compared to the rate at which their carbanions react with oxygen. 4-nitrotoluene is the least acidic but once the 4-nitrobenzyl anion is formed it reacts very quickly with oxygen. Ionisation of 2,4-dinitrotoluene is easier but the resulting anion is much less stable than the TNT anion and it too reacts quickly with oxygen. TNT is the most acidic compound of the three but in polar aprotic solvents the anion is greatly stabilised and reacts only slowly with oxygen.

It soon became clear that the reactions of 4-nitrotoluene and 2,4-dinitrotoluene with base and oxygen were complex and that significant differences in behaviour were apparent. Although useful information had been gained from this study of their reactivity it was obvious that a full understanding of the chemistry of TNT could not be gained using 4-nitrotoluene or 2,4-dinitrotoluene as model compounds.

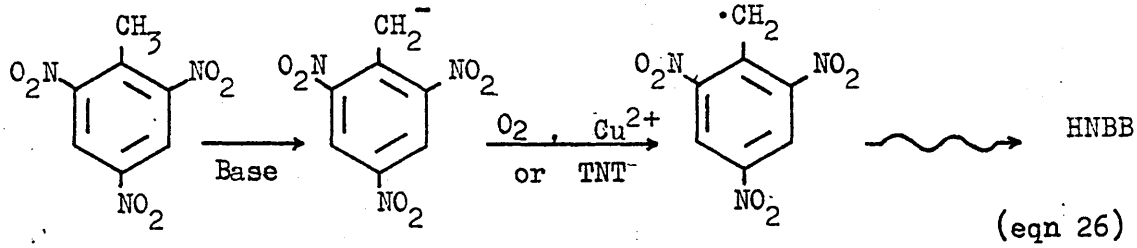
3.2.4 Mechanism

A mechanism to explain the formation of HNS and HNBB from oxidation of TNT in basic solution, must take into account the many intermediates (carbanions, complexes and radicals) that can be formed by the interaction of nitroaromatic compounds and base and assess the importance of each to the overall reaction. Other factors to be considered include the effect

of different solvents, the role of oxygen and the catalysis by metal ions.

The initial steps in the oxidative coupling of TNT to HNBB involved the fast formation of a 3- σ -complex and the subsequent, slower formation of TNT^-. The reaction went well in polar aprotic solvents because ionisation of TNT was promoted by good solvation of the TNT anion. Whether TNT^- was formed from the 3- σ -complex or directly from TNT was not clear.

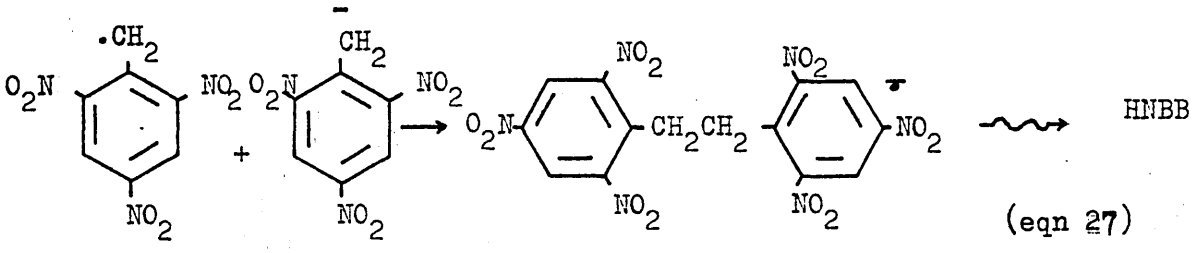
The presence of radicals in basic solutions of TNT has been demonstrated, although their precise structure is still unclear. An explanation of their origin is electron transfer between TNT^- and a suitable electron acceptor. The importance of oxygen and the effect of copper ions can be explained if these act as electron acceptors generating trinitrobenzyl radicals, which subsequently dimerise to HNBB. The small yield of HNBB from reactions performed under nitrogen arose because unionised TNT can also act as an electron acceptor, (eqn 26).



(eqn 26)

However, a similar mechanism which was invoked to explain the formation of 4,4' - dinitrobibenzyl (DNBB) from 4-nitrotoluene, was discounted because the rate of combination of 4-nitrobenzyl radicals with oxygen was expected to be greater than the rate of coupling. To produce the sort of yield of DNBB observed would require such a concentration of radicals that their reaction with oxygen would have to be explosive[14].

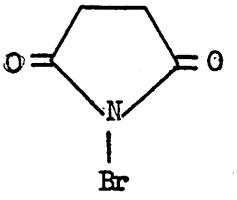
A n alternative radical mechanism involves the trapping of radicals by TNT^-, a reaction which could compete with the trapping of radicals by molecular oxygen[14] (eqn 27).



(eqn 27)

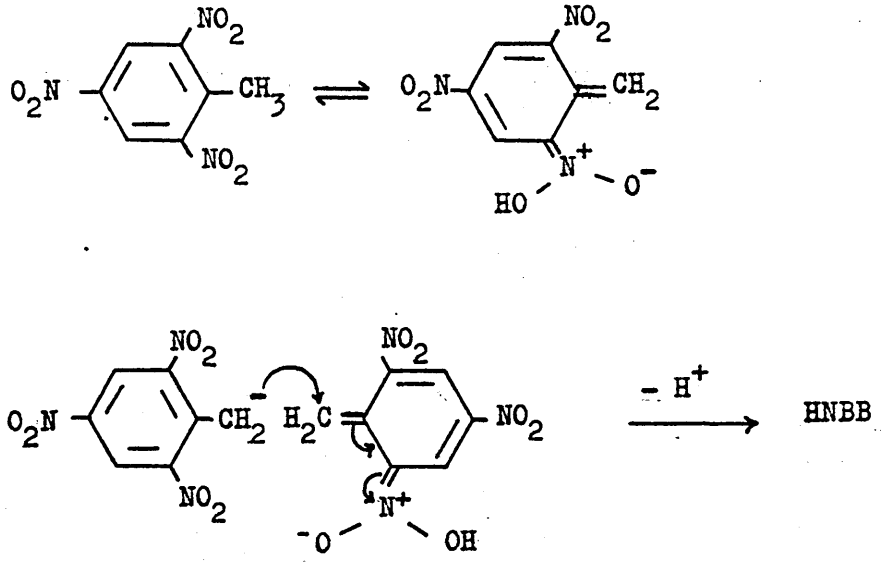
A radical mechanism was considered to explain the formation of HNBB and HNS from the Shipp Reaction[16]. Such a mechanism was rejected because these authors understood that TNT^- did not transfer an electron to oxygen to yield trinitrobenzyl radical under conditions where 4-nitrobenzyl anion readily forms 4-nitrobenzyl radical, which subsequently dimerises to the corresponding bibenzyl. It has, however, been shown that the formation of DNBB from 4-nitrotoluene can occur in the absence of oxygen[38], which complicates the comparison.

The detection of radicals does not necessarily mean that they are involved in the major reaction pathway in the system under study. Thus, even though N-bromosuccinimide (47) has been shown to give succinimidyl radicals, it seems that these are not involved to a major extent in the allylic bromination of alkenes[80].



(47)

An ionic mechanism was preferred to explain the Shipp Reaction and a similar sort of mechanism can be devised to explain the oxidation of TNT. Such a mechanism might involve nucleophilic attack by the trinitrobenzyl anion on aci-TNT (eqn 28).



(eqn 28)

Aci-forms of nitro compounds are well known and have been postulated as reaction intermediates[81], aci-TNT is thought to be an intermediate in the photochemical generation of the trinitrobenzyl anion[65]. The inadequacy of this mechanism is that it does not account for the effects of oxygen and catalyst.

Thus, on balance, the more likely mechanism is one which does involve electron transfer from TNT^- to an electron acceptor (eqn 26) with subsequent, rapid trapping of the intermediate radical by dimerisation (eqn 26) or, most probably, reaction with TNT^- (eqn 27). This mechanism is supported by the evidence produced in this study for the existence of TNT^- and the influence of oxygen and copper catalysts on the reaction.

Intramolecular dehydrogenations, such as the formation of HNS from HNBB, are thought to proceed via a mechanism involving ionisation and electron transfer reactions[54], (eqn 29).

$$PiCH_2\ CH_2Pi \xrightarrow{Base} Pi\bar{C}H\ \bar{C}H\ Pi \qquad (48)$$

$$Pi\bar{C}H\ \bar{C}HPi + \text{Electron Acceptor} \longrightarrow PiCH = CHPi^{\bullet\,-} \qquad (49)$$

$$PiCH = CHPi^{\bullet\,-} + \text{Electron Acceptor} \longrightarrow HNS$$

(eqn 29)

Now although there was evidence for the HNS radical anion (49), nothing like the dianion (48) was encountered in my experiments. Indeed, the results of exchange experiments suggested that ionisation of the methylene protons of HNBB did not occur to any extent.

It is difficult to see how the conversion of HNBB to HNS can proceed without ionisation of at least one of the methylene protons. The mechanism proposed to explain the dehydrogenation of HNBB to HNS by quinones used as its starting point removal of a methylene proton from HNBB followed by hydride abstraction by the quinone[42], (eqn 30).

$$PiCH_2\ CH_2Pi \xrightarrow{Base} PiCH_2\ \bar{C}HPi \qquad (50)$$

$$PiCH_2\ \bar{C}HPi + \text{quinone, Q} \longrightarrow HNS + QH^-$$

(eqn 30)

These authors presented preliminary spectroscopic evidence for the HNBB carbanion (50), but their spectrum most closely resembled that expected for a σ-complex of HNBB and cannot be taken as evidence for the existence of the carbanion.

There is evidence that electron transfer is a more efficient device for trapping carbanions than hydrogen-deuterium exchange[82]. Triphenylmethane (51) undergoes exchange of hydrogen for deuterium in deuterated t-butanol in the presence of potassium t-butoxide. The extent of deuterium

incorporation was 65% of one atom of deuterium. With nitrobenzene, a well-known electron acceptor, added to the reaction mixture the final product contained 7% of deuterated triphenylmethane and 58% of products arising from electron transfer with nitrobenzene, (eqn 31).

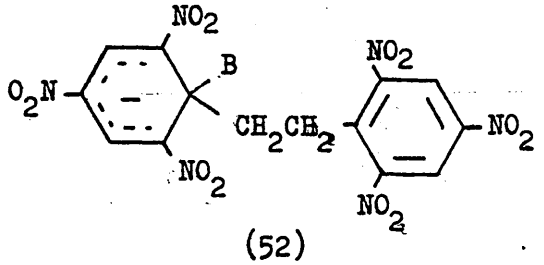
$$(C_6H_5)_3\,CH \longrightarrow (C_6H_5)_3\,C^- \xrightarrow{K_D} (C_6H_5)_3\,CD \quad (7\%)$$

$$(C_6H_5)_3\,C^- \xrightarrow{K_E} (C_6H_5)_3\,C\cdot \quad (58\%)$$

(51) (eqn 31)

The rate of electron transfer, K_E, was over eight times that for exchange K_D.

A mechanism for the formation of HNS might thus involve rapid production of an HNBB σ-complex (52), which is slowly converted to a carbanion (50), which then undergoes rapid electron transfer reactions to yield HNS. The rate of the electron transfer reactions being such that very little hydrogen-deuterium exchange is possible, (eqn 32).



(52)

$$\xrightarrow{\text{Slow}} \text{PiC}\bar{\text{H}}\ \text{CH}_2\text{Pi} + \text{HB}$$

(50)

$$\text{PiC}\bar{\text{H}}\ \text{CH}_2\text{Pi} + O_2 \text{ or } Cu^{2+} \xrightarrow{\text{fast}} \text{PiC}\dot{\text{H}}\ \text{CH}_2\text{Pi}$$

$$\text{PiC}\dot{\text{H}}\ \text{CH}_2\text{Pi} \xrightarrow{-\text{H}\cdot} \text{PiCH} = \text{CHPi}$$

(eqn 32)

HNS itself could be involved in electron transfer reactions with the carbanion (50), being converted in the process to the HNS radical anion, (49, eqn 33).

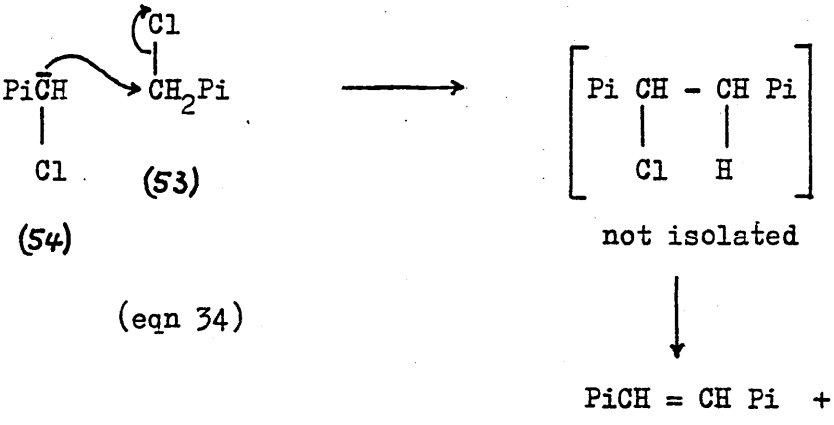
$$PiC\bar{H}\,CH_2Pi \;+\; PiCH=CHPi \longrightarrow Pi\dot{C}H\,CH_2Pi \;+\; PiCH=CHPi^{\cdot-}$$

(50) (eqn 33) (49)

The driving force for the expulsion of a hydrogen atom, in the final step of the mechanism, is the formation of the double bond in HNS.

3.2.5 A Comparison of the Hungarian and Shipp Reactions

The mechanism of formation of HNS by the Hungarian reaction appears to involve radical intermediates. A radical mechanism to explain the Shipp reaction was discounted in favour of an ionic mechanism involving bimolecular displacement of the halide ion of 2,4,6-trinitrobenzyl chloride (53), an intermediate in the reaction, by the α-chlorotrinitrobenzyl carbanion[16], (54, eqn 34).



(eqn 34)

The reaction of 4-nitrobenzyl chloride with strong bases yields 4,4'-dinitrostilbene by a mechanism consistent with radical anion intermediates[83]. A similar mechanism to explain the formation of HNS from 2,4,6-trinitrobenzyl chloride is shown below, (eqn 35).

$$PiCH_2Cl + Base \longrightarrow Pi\bar{C}HCl$$

$$PiCH_2Cl + Base \longrightarrow PiCH_2Cl^{\cdot-}$$

$$PiCH_2Cl^{\cdot-} \longrightarrow PiCH_2^{\cdot} + Cl^-$$

$$PiCH_2^{\cdot} + Pi\bar{C}HCl \longrightarrow PiCH_2CHClPi^{\cdot-}$$

$$PiCH_2CHClPi^{\cdot-} + PiCH_2Cl \longrightarrow PiCH_2Cl^{\cdot-} + PiCH_2CHClPi$$

$$PiCH_2CHClPi \longrightarrow PiCH=CHPi + HCl$$

(eqn 35)

So the mechanism of both the Hungarian and Shipp reactions may be similar, involving carbanion and radical anion intermediates.

Both methods involve the reaction of TNT with base, can be modified to give good yields of HNBB, and are complicated by side reactions yielding a variety of by-products. The need for a metal catalyst in the Hungarian method makes it less simple than the Shipp process and complicates solvent recovery and recycling which would be necessary to make the method economic. The need to heat the reaction mixture also pushes up the cost of the Hungarian process.

The yield from both reactions is similar and cannot justify replacing the established Shipp method. The Hungarian reaction does have the advantage that it can be used to prepare HNS from HNBB, this is not possible with the Shipp method. A 'Dual Synthesis' has been investigated at PERME in which HNBB produced in good yield from the Shipp process is oxidised to HNS by the Hungarian method[73]. Another approach has been to treat the by-products from the Shipp process with the Hungarian process thus increasing the yield of HNS and cleaning up a complex mixture of waste products.

3.2.6 Summary

The synthesis of HNS by the Hungarian Patent method has been investigated in two parts: (i) the conversion of TNT to HNBB; (ii) the formation of HNS from HNBB. The influence on these reactions of various parameters (base, solvent, oxygen and catalyst) has been studied.

At room temperature, basic solutions of TNT in polar aprotic solvents absorb oxygen to yield HNBB, along with small amounts of other, more polar by-products, the identities of which are uncertain. The best yield of HNBB was obtained using sodium methoxide as base in an equimolar amount with TNT. The yield of HNBB was increased by using a copper sulphate-pyridine catalyst and less oxygen was absorbed. Other catalysts which improved the

reaction included the precipitate obtained from reaction of copper sulphate in DMF with methanolic potassium hydroxide.

Warming a basic solution of HNBB, in a polar aprotic solvent, to 55°C yielded HNS as the main product. Again the reaction was improved by the use of a copper catalyst, but in contrast to the oxidation of TNT, less base was required and oxygen was not necessary for the reaction to proceed.

Solutions of 4-nitrotoluene, in the presence of base, absorbed oxygen more quickly than TNT and the predominant product was 4,4'-dinitrostilbene. Visible spectroscopy established that the 4-nitrotoluene radical anion was an intermediate. A basic solution of 2,4-dinitrotoluene took up oxygen more readily than 4-nitrotoluene and the reaction was marked by a green colour due to the 2,4-dinitrobenzyl anion. An explanation for the different oxidation behaviour of the three nitrotoluenes has been given.

Consideration of the results of this study has led to the suggestion, from the evidence, that the mechanism to explain the formation of HNBB and HNS from TNT involves the intermediacy of carbanions, radicals and radical anions. The results could not justify replacement of the established Shipp method of HNS production with the Hungarian Patent method.

4. EXPERIMENTAL

HNBB and HNS, like TNT are explosives and may detonate on grinding or impact.

4.1 Storage and Use of Explosives

Normally work with explosives is subject to licensing through the Explosives Act which is now subsidiary legislation to the Health and Safety at Work Act. The Health and Safety Executive were contacted to establish whether a licence was necessary for this work.

After discussions with the Establishment Safety Officer, PERME (Waltham Abbey) and the Director of Studies, H.M. Inspector of Explosives gave an assurance in writing that in view of the small quantities of explosives involved a licence would not be necessary. However, a certificate to keep explosives was obtained from the district Chief Office of Police.

Storage

PERME, Waltham Abbey, supplied up to 200g of TNT at a time, along with smaller amounts of HNBB and HNS. The explosives were supplied wetted with water and packed in plastic bottles, 10g to the bottle. The bottles were contained in an ammunition box. This box was kept in an unmarked yellow metal cabinet bolted to the bench in the laboratory.

The cabinet was locked and keys kept by the Director of Studies and the research student. Additions and removals to and from the cabinet were noted in a log book.

Experimental Procedure

Only sufficient explosive necessary for each experiment, not usually more than 1g, was removed from the store at any one time. It was filtered and recrystallised. All filtrates and washings were added to an explosives waste bucket.

To avoid friction and unnecessary contact with metals, plastic or bone spatulas were used to handle sensitive materials. Filtering of solutions of explosives was carried out with plastic sinters. When apparatus with ground glass joints had to be used the joints were covered with plastic sleeves.

No flames were used in the vicinity of sensitive material. Products from reactions were dried under vacuum, never heated in an oven.

Spillages were immediately swabbed up, the affected area drenched with water and the water washings swabbed up. The swabs were discarded into the explosives waste bucket.

Waste Disposal

Residues from experiments were stored under water in a plastic bucket lined with a plastic bag. The bucket was labelled and stored in a fume cupboard. With time most organic solvents evaporated leaving any explosive material dispersed in water.

Arrangements were made with PERME for the waste to be collected from time to time, returned to PERME at Waltham Abbey and disposed of by burning.

4.2 Materials

TNT was supplied by PERME, wetted with water. It was filtered, washed with methanol and recrystallised from methanol. The pale cream coloured needles melted at 81-82°C, (lit. m.p. 82°C[84]).

HNBB was supplied by PERME, wetted with water. It was filtered and dried under vacuum. The material was recrystallised by dissolving it in hot acetone, filtering the hot solution, adding hot water to the cloud point and chilling. The pale yellow needles melted at 226-227°C, (lit. m.p. 218-220°C[16]).

HNS was supplied by PERME, wetted with water. It was filtered and washed thoroughly with acetone. The pale yellow needles melted with decomposition at 315°C, (lit. m.p. 316°C dec.[12]).

4-Nitrotoluene - laboratory reagent grade material was recrystallised from ethanol, melting point 51-52°C, (lit. m.p. 52-54°C[84]).

2,4-Dinitrotoluene was prepared by nitration of 4-nitrotoluene[85]. Into a 250 cm^3 round bottom flask were poured fuming nitric acid (12 cm^3) and concentrated sulphuric acid (16.5 cm^3). 4-Nitrotoluene (14g, 1 x 10^{-1} mol.) was added in small portions such that the temperature of the mixture did not exceed 50°C. A small funnel was placed in the mouth of the flask and the flask heated on a water bath at 90-95°C for 30 mins. The mixture was then cooled and slowly poured into ice-water (500 cm^3). The resulting precipitate was filtered at the pump, washed well with water and recrystallised from methanol. The yield was 60% of theoretical and the melting point of the product 69-70°C, (lit. m.p. 70.2°C[84]).

Solvents

DMF and DMSO were stored over molecular sieve 4A and then distilled under reduced pressure when required. Methanol was dried over molecular sieve 3A and distilled prior to use. THF and toluene were sodium dried and distilled. Pyridine was dried with potassium hydroxide and distilled when needed. Petroleum spirit (40°-60°) and ethyl acetate were distilled before use.

Catalysts

Anhydrous copper sulphate was prepared by gently heating Analar hydrated copper sulphate. It was stored in an oven at 150°C. The copper-pyridine complex, $(Cu\ (pyridine)_2)_2$ SCN was prepared by the method of Vogel[88]. Ferric chloride, cuprous and cupric chloride were all reagent grade and used without further purification.

Bases

Methanolic potassium hydroxide was prepared by dissolving Analar potassium hydroxide in dry, distilled methanol. Sodium methoxide solution was prepared by dissolving clean, bright sodium in dry, distilled methanol. Potassium t-butoxide solution was prepared from commercially available potassium t-butoxide. Tetramethylammonium hydroxide in methanol was also the commercially available product.

Base concentration was determined by titration with standard hydrochloric acid solution using phenolthalein indicator.

Sodium hydride, as a disperson in oil and Proton Sponge were used as received.

4.3 The Hungarian Patent Method - A Typical Reaction

Anhydrous copper sulphate (0.1g, 6.3×10^{-4} mol.) was weighed into a 100 cm^3, two-neck, round bottom flask and mixed with pyridine (1 cm^3) and DMF (4 cm^3) for five minutes using a magnetic stirrer. TNT (0.45g, 2×10^{-3} mol.) and more DMF (5 cm^3) were added and when the TNT had dissolved the flask was flushed with oxygen. 1.9M methanolic potassium hydroxide (1 cm^3, 1.9×10^{-3} mol.) was added. The mixture was stirred vigorously, with oxygen passing through the flask at 500 $cm^3\ min^{-1}$, for the duration of the reaction. After 30 minutes the mixture was poured into dilute hydrochloric acid (50 cm^3). The resulting precipitate was filtered, washed with water and dried under vacuum. The product (0.36g) at this stage was shown by ^{1}HNMR analysis, to consist of 0.27g of HNBB, equivalent to 60% of the theoretical yield.

If the reaction mixture was warmed to 55°C for 15 minutes before pouring into acid and then the crude product washed with acetone, 0.18g of HNS was isolated, equivalent to 40% of the theoretical yield.

4.4 The Measurement of Oxygen Uptake

Oxygen uptake was measured using the simple apparatus shown in Fig. 3.6. The apparatus was flushed with oxygen then filled with the gas and the pressure inside the system adjusted to atmospheric pressure by levelling the water in the two arms of the manometer. The base was added to the solution of nitroaromatic compound by inverting the sidearm, then the clock and the stirrer were started. The oxygen uptake was followed at atmospheric pressure by manually keeping the water in the two arms of the manometer at the same level.

4.5 Product Analysis

4.5.1 Chromatography

The crude reaction products were investigated by a variety of chromatographic techniques.

Thin Layer Chromatography (TLC) Commercial, plastic-backed, silica plates, thickness 0.25 mm, containing a fluorescent indicator were used. A mixture of 40% ethyl acetate in 40-60 petroleum ether gave a good separation of TNT, HNBB and many of the by-products of the reactions, but left HNS on the baseline of the plate. HNS could be eluted with toluene containing a few drops of DMF. Visualisation was by UV light at 254 nm.

Column Chromatography Short path-length chromatography columns[86] of TLC grade silica were used to separate HNBB and other components from crude reaction products, 20% ethyl acetate in 40-60 petroleum ether acidified with a drop of glacial acetic acid was used as eluent. Elution of the various components was followed by TLC.

High Performance Liquid Chromatography (HPLC) HPLC was carried out on a Microporosil column, $\frac{1}{3}$ metre long, 5 micron particle size. The solvent system consisted of:

cyclohexane (13 parts); tetrahydrofuran (9 parts);

DMSO (3 parts); ethanol (0.25 parts).

Loop injection and UV (254 nm) detection were used.

4.5.2 TLC/Visible Spectrometry[70]

About 0.1g of dry, crude reaction product was accurately weighed then dissolved in tetrahydrofuran and the solution made up to 25.00 cm^3 volume. 25 µl of this solution was applied to a silica TLC plate from a micro-pipette. A guide spot of a mixture of TNT, HNBB and HNS was spotted separately at the origin at the same time. The plate was eluted in toluene-DMF (50:1), dried in air and the zones of interest visualised under UV light at 254 nm.

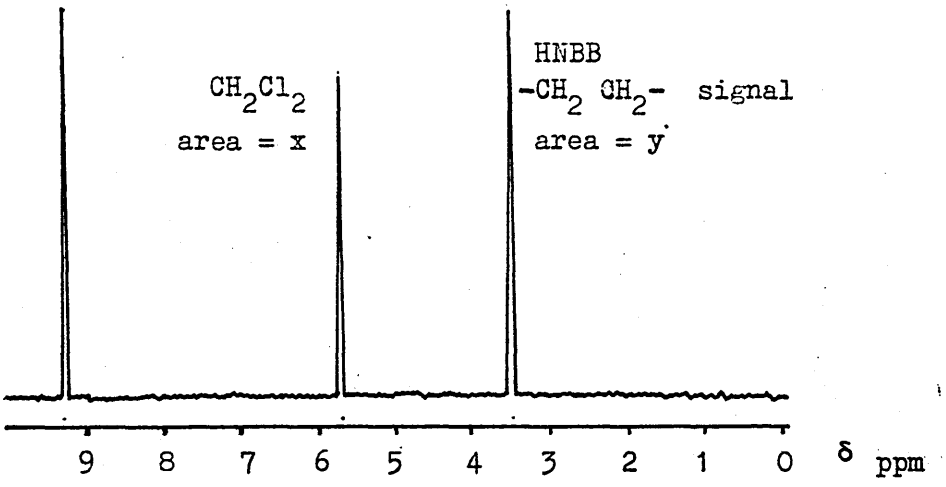
The HNBB zone was scraped from the plate and extracted with DMSO (4 x 1 cm^3). The silica was filtered off and then ethylenediamine (0.1 cm^3) added to the extract and the volume of the solution made up to 10.00 cm^3 with more DMSO. The absorbance of this solution was measured at 465 nm against a blank solution prepared from a clean part of the original TLC plate. The concentration of HNBB was obtained from a calibration curve prepared from samples of known HNBB content.

TNT and HNS could also be analysed in this manner.

4.5.3 Quantitative ^{1}HNMR

About 25 mg of crude product was accurately weighed then dissolved in acetone-D_6. Dichloromethane (5 µl) was added to this solution from a micropipette and then the ^{1}HNMR spectrum of the solution recorded. The integration of the HNBB methylene protons signal (δ 3.5 ppm) was measured and compared with the integration of the signal due to the dichloromethane protons.

The signal area for 1 mol. of protons could be calculated from the signal produced by the known amount of dichloromethane hence the number of moles of HNBB present could be derived, (Fig. 4.2).



mols. CH_2Cl_2 = X

area CH_2Cl_2 signal = x

area HNBB signal = y

$$\text{area/mol. H} = \frac{x}{2X}$$

$$\text{No. of mols. H giving signal of area } y = \frac{x}{2X} \cdot y$$

HNBB contains 4 methylene H's $\therefore$

$$\text{No. mols. HNBB} = \frac{x}{2X} \cdot \frac{y}{4}$$

Fig. 4.2 Quantitative analysis by ^{1}HNMR

4.6 Hydrogen-Deuterium Exchange

A reaction mixture containing HNBB (2.4×10^{-1} mol.dm.$^{-3}$) and sodium methoxide-D_3 (2.4×10^{-1} mol.dm.$^{-3}$) in 90/10 DMF/methanol-D_4 at 55°C, was quenched in 50% acetic acid-D_4 in D_2O, 1 min. after mixing the reactants. The resulting precipitate was filtered, and recrystallised from acetic acid. The deuterium content of this recovered HNBB was deduced by mass spectrometry, infra-red and ^{1}HNMR spectroscopy.

Mass Spectrometry HNBB undergoes a simple fission process in the mass spectrometer to produce an abundant ion at $^m/_e$ 226. The abundance of the carbon-13 peak associated with this ion was 10% of the peak at $^m/_e$ 226 for HNBB but it increased to 60% for the HNBB recovered from the exchange experiment, (Fig. 2.8). Deuterium had been incorporated into the recovered HNBB.

Infra-Red A new absorption band in the spectrum of the recovered HNBB occurred around 2300 cm^{-1}, close to the value expected for the C-D stretching frequency if an aromatic proton of HNBB, stretching frequency 3100 cm^{-1}, had been replaced by deuterium, Fig. 2.9.

^{1}HNMR An accurate weight of recovered HNBB (approx. 17 mg.) was dissolved in a known volume of deuterated acetone (around 0.5 cm^3) spiked with 1% dichloromethane as an internal standard. The ^{1}HNMR of this solution was recorded with integration. The areas of the aromatic (δ 9.1 ppm) and methylene (δ 3.4 ppm) proton signals were compared to the area of the dichloromethane signal (δ 5.6 ppm) and these figures compared to the ratios found in the spectrum of the same weight of HNBB recorded under the same conditions.

	HNBB	Recovered HNBB
Ar-H/CH_2Cl_2	1.10	0.76
$-CH_2CH_2-$/CH_2Cl_2	1.10	1.00

4.7 Electrochemical Methods

4.7.1 Tetraethylammonium Perchlorate (TEAP) Supporting Electrolyte[87]

A hot, aqueous solution of tetraethylammonium chloride (1 mol.dm.$^{-3}$, 50 cm^3) was mixed with a hot, aqueous solution of sodium perchlorate (1 mol.dm.$^{-3}$, 50 cm^3). The mixture was cooled in iced water and the resulting precipitate filtered and washed with ice-cold water until chloride-free (silver nitrate test). The product was dried overnight in a vacuum oven at 50°C and then stored in a dessicator over silica gel.

4.7.2 Polarography and Electrolysis

A commercial polarograph was used with a dropping mercury electrode and a reference electrode consisting of a silver wire in a solution of TEAP (1×10^{-1} mol.dm.$^{-3}$) in DMF, the reference electrode was separated from the solution under test by a liquid-liquid junction. The supporting electrolyte in each case was TEAP (1×10^{-2} mol.dm.$^{-3}$). The results are presented in Table 4.1.

The cell used for electrolysis is shown in Fig. 2.10. TEAP (1×10^{-2} mol.dm.$^{-3}$ for HNBB and HNS, 4.8×10^{-2} mol.dm.$^{-3}$ for TNT) was the supporting electrolyte. The polarograph was readily adapted for use as a potentiostat. A sample of the solution under electrolysis was removed and its visible spectrum recorded. The results are presented in Table 4.2.

4.8 Instrumentation

^{1}HNMR measurements were made with Jeol C-60 HL or Varian EM 360 A instruments using tetramethylsilane as reference. Mass spectra were recorded on an AEI MS 30 instrument. Visible spectral measurements were made with Unicam SP 800A, infra-red spectra were recorded on a Unicam SP 1200. HPLC was carried out using a Waters Associates Liquid Chromatograph with a Perkin Elmer LC 55 Variable Wavelength Detector. A PAR 174 Polarographic Analyser was used for polarography and electrolysis.

Table 4.1 Polarography Results

Compound	Conc./mol.dm.$^{-3}$	$E_{\frac{1}{2}}$/V
TNT	1.5×10^{-4}	-0.47, -1.00, -1.25
HNBB	2.4×10^{-4}	-0.40, -0.95, -1.32
HNS	2.4×10^{-4}	-0.6 -1 (i), -1.2 (i)

(i) ill defined

Table 4.2 Controlled Potential Electrolysis

Compound	Conc./mol.dm.$^{-3}$	Electrolysis Potential/V	λ Max of Product/nm
TNT	4.3×10^{-2}	-0.6	520, 630
HNBB	4.5×10^{-3}	-0.6	438, 525
HNS	2.4×10^{-4}	-0.7	610

5. SUMMARY AND CONCLUSIONS

HNS is a heat resistant explosive which is also important as a crystal growth modifier for melt-cast TNT. The publication of a Hungarian patent claiming a new method of preparation of HNS by catalytic oxidation of TNT, was of particular interest since the present process is not without problems. This research project, carried out in collaboration with the Ministry of Defence, PERME (Waltham Abbey), has studied this new reaction to identify the parameters which are significant and to contribute to an understanding of the mechanism involved.

Visible and ^{1}HNMR spectroscopy, hydrogen-deuterium exchange experiments and electrochemical methods have been used to identify the intermediates involved in the synthesis of HNS by the Hungarian reaction. In a typical reaction a variety of colours is produced, the reaction mixture changes from brown to purple to red-brown and then blue. These colours have been assigned to a 3-σ-complex of TNT, TNT^-, 1- and 3-σ-complexes of HNBB and the HNS radical anion, respectively. In addition it was observed that the reaction of HNS with base yielded a σ-complex. The intermediates from HNBB and HNS have not been previously reported.

Visible spectroscopy was used to assign the transient brown colour to a 3-σ-complex of TNT and the purple colour to TNT^-. Similarly, the red-brown was recognised as a σ-complex of HNBB, ^{1}HNMR provided the evidence to show that initially a 3-σ-complex was produced which then converted to the thermodynamically more stable 1-σ-adduct. The identity of the blue species was not clear at this stage but ^{1}HNMR implied the presence of radicals in the system.

The possibility of the involvement of a carbanion of HNBB in the reaction was tested by hydrogen-deuterium exchange methods. It was shown that HNBB did ionise in basic solution, but loss of an aromatic proton not

a methylene proton, occurred. Evidence of exchange was provided by mass spectrometry and infra-red and quantitative ^{1}HNMR spectroscopy. Around 1 in 4 of the aromatic protons of HNBB had been replaced by deuterium. Hydrogen-deuterium exchange from HNBB in basic solution has not been reported before.

Controlled potential electrolysis of a solution of TNT produced TNT^- as the predominant product, with HNBB the product was a σ-complex. Instability of the initial radical anions was thought to be the source of these products. However, electrolysis of a solution of HNS produced a blue colour with a visible spectrum which matched that seen in the final stages of the oxidation reaction under study. This species, which was not generated in basic solutions of HNS, was assigned as the HNS radical anion.

At room temperature HNBB was the main product of the oxidation of TNT, with HNS produced when the reaction mixture was warmed to 55°C. There were significant differences between the products of catalysed and uncatalysed reactions. At least five other, minor components, in addition to TNT, HNBB and HNS, were separated by thin-layer chromatography from the products of uncatalysed reactions. A cleaner product was obtained from catalysed reactions. None of the by-products were identified due to their instability or low concentration.

The best yield of HNBB was obtained using sodium methoxide in reactions containing one mole of base for each mole of TNT. The reaction went well in polar aprotic solvents which promote the ionisation of TNT by solvation of the anion and in which hydroxide or methoxide ions are highly reactive.

Although some HNBB was formed under a nitrogen atmosphere, oxygen was vital to obtain a good yield. Oxygen uptake was reduced and a better yield of HNBB obtained when cupric ions were present. A variety of copper catalysts were investigated with varying results, but for ease of preparation and removal at the end of the reaction, the copper sulphate-pyridine slurry

was preferred. The dehydrogenation of HNBB to HNS was also improved using copper ions but, in contrast to the formation of HNBB from TNT, less base was required and the reaction could proceed successfully in the absence of oxygen.

A comparison of the oxidation behaviour of basic solutions of 4-nitrotoluene and 2,4-dinitrotoluene with that of TNT, showed that there were distinct differences between these compounds. It was proposed that the explanation lay in the relative acidities of these compounds and the reactivity of their carbanions. The less hazardous nitrotoluenes do not behave as models of the TNT system.

The mechanism of the conversion of TNT to HNBB involved the fast formation of a 3- σ-complex and subsequent slower formation of TNT^-. The importance of oxygen and the effect of copper ions is explained by a mechanism in which they act as electron acceptors, generating trinitrobenzyl radicals which dimerise to HNBB or are trapped by TNT^-. Unionised TNT can also act as an electron acceptor. The formation of HNS from HNBB is considered to proceed via a mechanism involving rapid formation of a σ-complex of HNBB which slowly converts to a carbanion which then undergoes rapid electron transfer to yield HNS by loss of a hydrogen atom. HNS itself can take part in these electron transfer reactions to yield the HNS radical anion and the blue colour of the reaction mixture.

The results from this study have made a contribution towards understanding the chemistry of the conversion of TNT to HNBB and HNS by the Hungarian patent method. Evidence has been presented for the formation of a variety of intermediates during the course of the reaction, some of which have not previously been reported. The important parameters affecting the reaction have been discovered and a probable mechanism proposed. Although the Hungarian patent method of HNS production is comparable in efficiency to the established Shipp process, it shows no particular advantages which could justify replacing the present method.

REFERENCES

1. N.J. Bowman, E.F. Knippenberg, J. Spacecraft, 1966, 3, 1542.
2. E.E. Kilmer, J. Spacecraft, 1968, 5, 1216.
3. T. Urbanski, S.K. Vasudeva, J. Sci. Ind. Res., 1978, 37, 250.
4. J.S. Back, J.L. Soderberg, C.L. Hakanson, Fr. Demande, 2, 007, 049 (Chem. Abs. 73, 27153).
5. J.R.C. Duke, paper presented at a Symposium on the Chemistry of Hexanitrostilbene, Ministry of Defence, P.E.R.M.E., Waltham Abbey, 1979.
6. S. Trevino, ibid.
7. M.A. Parry, B.W. Thorpe, J. Crystal Growth, 1979, 47, 541.
8. F. Challenger, P.H. Clapham, J. Chem. Soc., 1948, 1612.
9. A.H. Blatt, A.W. Rytina, J. Am. Chem. Soc., 1950, 72, 403.
10. J. Thiele, R. Escales, Ber. Dt. Chem. Ges., 1901, 34, 2846.
11. F. Ullman, M. Gschwind, Ber. Dt. Chem. Ges., 1908, 41, 2296.
12. K.G. Shipp, J. Org. Chem., 1964, 29, 2620.
13. A.G. Green, A.H. Davies, R.M. Horsfall, J. Chem. Soc., 1907, 91, 2079.
14. G.A. Russell, A.J. Moye, E.G. Janzen, S. Mak, E.R. Talaty, J. Org. Chem., 1967, 32, 137.
15. S. Reich, O. Wetter, M. Widmer, Ber. Dt. Chem. Ges., 1912, 45, 3055.
16. K.G. Shipp, L.A. Kaplan, J. Org. Chem., 1966, 31, 857.
17. T. Kompolthy, G. Bencz, J. Deres, L. Hajos, Hungarian Patent, T/9639 (Chem. Abs., 84, 58886).
18. E. Buncel, A.R. Norris, K.E. Russell, Quart. Rev., 1968, 22, 123.
19. M.R. Crampton, Adv. Phys. Org. Chem., 1969, 7, 211.
20. P. Buck, Angew. Chem. Int. Ed., 1969, 8, 120.
21. E.F. Caldin, G. Long, Proc. Roy. Soc. A, 1955, 228, 263.

22. K. Bowden, R. Stewart, Tet., 1965, 21, 261.

23. R.E. Miller, W.F.K. Wynne-Jones, J. Chem. Soc., 1961, 4886.

24. E. Buncel, K.E. Russell, J. Wood, Chem. Comm., 1968, 252.

25. C. Bernasconi, J. Org. Chem., 1971, 36, 1671.

26. E. Buncel, A.R. Norris, K.E. Russell, R. Tucker, J. Am. Chem. Soc., 1972, 94, 1646.

27. E. Buncel, A.R. Norris, K.E. Russell, P. Sheridan, H. Wilson, Can. J. Chem., 1974, 52, 1750.

28. E. Buncel, A.R. Norris, K.E. Russell, H. Wilson, Can. J. Chem., 1974, 52, 2306.

29. K.L. Servis, J. Am. Chem. Soc., 1967, 89, 1508.

30. C.A. Fyfe, C.D. Malkiewich, S.W.H. Damji, A.R. Norris, J. Am. Chem. Soc., 1976, 98, 6983.

31. R. Schaal, J. Chim. Phys., 1955, 52, 796.

32. R. Schaal, G. Lambert, J. Chim. Phys., 1962, 59, 1151.

33. J.B. Ainscough, E.F. Caldin, J. Chem. Soc., 1956, 2546.

34. D.N. Brooke, M.R. Crampton, J. Chem. Res. (S), 1980, 340.

35. E. Buncel, A.R. Norris, W. Proudlock, Can. J. Chem., 1968, 46, 2759.

36. J.A. Chudek, R. Foster, J. Chem. Soc. Perkin II, 1979, 628.

37. D.N. Brooke, M.R. Crampton, G.C. Corfield, P. Golding, G.F. Hayes, J. Chem. Soc. Perkin II, 1981, 526.

38. G.A. Russell, E.G. Janzen, J. Am. Chem. Soc., 1962, 84, 4153.

39. G.A. Russell, E.G. Janzen, J. Am. Chem. Soc., 1967, 89, 300

40. S.H. Glarum, T.H. Marshall, J. Chem. Phys., 1964, 41, 2182.

41. D.J. Glover, E.G. Kayser, Analyt. Chem., 1968, 40, 2055.

42. G.P. Sollot, M. Warman, E.E. Gilbert, J. Org. Chem., 1979, 44, 3328.

43. R.J. Pollitt, B.C. Saunders, Proc. Chem. Soc., 1962, 176.

44. R. Foster, R.K. Mackie, Tet., 1963, 19, 691.

45. E. Buncel, A.W. Zabel, J. Am. Chem. Soc., 1967, 89, 3082.

46. M.R. Crampton, V. Gold, J. Chem. Soc. (B), 1966, 498.

47. E. Buncel, J.A. Elvidge, J.R. Jones, K.T. Watkin, J. Chem. Res. (S), 1980, 272.

48. E. Buncel, E.A. Symons, J. Org. Chem., 1973, 38, 1201.

49. R.D. Allendoerfer, P.H. Rieger, J. Am. Chem. Soc., 1966, 88, 3711.

50. J.G. Lawless, D.E. Bartak, M.D. Hawley, J. Am. Chem. Soc., 1969, 91, 7121.

51. H.D. Burrows, E.M. Kowsower, J. Phys. Chem., 1974, 78, 112.

52. J.M. Milliner, H. Pobiner, Analyt. Chem., 1964, 36, 238.

53. G. Scott, Atmospheric Oxidation and Autoxidation, 1965, Elsevier.

54. G.A. Russell, E.G. Janzen, A.G. Bemis, E.J. Geels, A.J. Moyes, S. Mak, E.T. Strom, ACS Adv. in Chem., 1965, 51, 112.

55. G.N. Schrauzer (Editor), Transition Metals in Homogeneous Catalysis, 1971, Marcel Dekker Inc.

56. H. Pines, B. Kvetinskas, V.N. Ipatieff, J. Am. Chem. Soc., 1955, 77, 343.

57. G.A. Russell, G. Kaupp, J. Am. Chem. Soc., 1969, 91, 3851.

58. M. Kharasch, G. Sosnovsky, Tet., 1958, 3, 97.

59. H.A.P. De Jongh, C.R.H.I. De Jonge, W.J. Mijs, J. Org. Chem., 1971, 36, 3160.

60. M.W. Rathke, A. Lindert, J. Am. Chem. Soc., 1971, 93, 4605.

61. H. Finkbeiner, A.S. Hay, H.S. Blanchard, G.F. Endres, J. Org. Chem., 1966, 31, 549.

62. H.A. Stansbury, W.R. Proops, J. Org. Chem., 1961, 26, 4162.

63. N. Rabjohn, Org. Synth. Collect. Vol. V, Wiley, New York, 1963, 517.

64. N.E. Burlinson, L.A. Kaplan, C.E. Adams, Naval Ordnance Lab., AD-769-670.

65. N.E. Burlinson, M.E. Sitzman, L.A. Kaplan, E. Kayser, J. Org. Chem., 1979, 44, 3695.

66. J.C. Dacons, H.G. Adolph, M.J. Kamlett, J. Phys. Chem., 1970, 74, 3035.

67. R.N. Rogers, Analyt. Chem., 1967, 39, 730.

68. F. Cuta, E. Beranek, Colln. Czech. Chem. Comm., 1974, 39, 736.

69. K.G. Shipp, L.A. Kaplan, M.E. Sitzmann, J. Org. Chem., 1972, 37, 1966.

70. J.C. Hoffsommer, J.F. McCullough, J. Chromat., 1968, 38, 508.

71. A.J. Parker, Quart. Rev., 1962, 16, 163.

72. M. Fieser, L.F. Fieser, Reagents for Organic Synthesis.

73. P. Golding, G.F. Hayes, A. Saunders, P.E.R.M.E. Technical Report 108.

74. F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edn., Wiley-Interscience, 1972, 914.

75. K. Nakamoto, Infra-red and Raman Spectra of Inorganic and Co-ordination compounds, 3rd Edn., Wiley-Interscience, 1978, 241.

76. I. Bodek, G. Davies, Inorg. Chem., 1978, 17, 1814.

77. H. Praliaud, Y. Kodratoff, G. Coudurier, M.V. Mathieu, Spectrochim. Acta., 1974, 30A, 1389.

78. G. Coudurier, H. Praliaud, M.V. Mathieu, Spectrochim. Acta., 1974, 30A, 1399.

79. R.J. Pollitt, B.C. Saunders, J. Chem. Soc., 1965, 4615.

80. D.C. Nonhebel, J.C. Walton, Free-Radical Chemistry, Cambridge, 1974, 53.

81. A.T. Nielsen, H. Feuer (Editor), The Chemistry of the Nitro- and Nitroso- Groups Part 1, Chapter 7, Interscience, 1969.

82. R.D. Guthrie, J. Am. Chem. Soc., 1969, 91, 6201.

83. D. Bethell, R. Bird, J. Chem. Soc. Perkin II, 1977, 1856.

84. J.R.A. Pollock, R. Stevens (Editors), Dictionary of Organic Compounds, 4th Edn., Eyre and Spotiswoode Ltd., London 1965.

85. A.I. Vogel, Practical Organic Chemistry, 3rd Edn., Longmans, 1961, 527.

86. B.J. Hunt, W. Rigby, Chem. and Ind., 1967, 1868.

87. I.M. Kolthoff, J·F. Coetzee, J. Am. Chem. Soc., 1957, 79, 870.

88. A.I. Vogel, Quantitative Inorganic Analysis, 2nd Edn., Longmans Green and Co., 1955, 432.

POSTGRADUATE STUDIES

Postgraduate studies have included a short lecture course on catalysis by Dr. White of the University of Sheffield along with other lectures and research colloquia at the University and Sheffield City Polytechnic.

The annual meetings of the Chemical Society Organic Reaction Mechanisms Discussion Group were attended at Bangor in 1978 and Brighton in 1979, along with an International Symposium on the Chemistry of HNS at PERME, Waltham Abbey. The SRC Graduate School was attended in 1979.

As part of the SRC CASE Studentship three months of the project were spent working at the collaborating establishment, PERME, Waltham Abbey.

Dr. Corfield presented papers on part of this thesis at the symposium on HNS at PERME in 1979 and at the 5th IUPAC Conference on Physical Organic Chemistry at Santa Cruz, California in 1980. A paper containing some of the results of this research has been submitted to the Journal of the Chemical Society, Perkin II.

Membership of the Royal Society of Chemistry was awarded as a result of counselled experience over the duration of this research project.